Quantum-well-width dependencies of postgrowth thermal annealing effects of InGaN/GaN quantum wells

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Optical measurements of temperature-dependent photoluminescence (PL) spectral peak, integrated PL intensity and PL decay time, and microstructure analyses with high-resolution transmission electron microscopy showed the strong dependencies of thermal annealing effects on quantum well (QW) width in InGaN/GaN QW structures. With different QW widths, different levels of strain energy were built. Upon thermal annealing, energy relaxation resulted in the reshaping of quantum dots and hence the changes of optical properties. Thermal annealing at 800 °C of a narrow QW width (2 nm) structure led to regularly distributed quantum dots (QDs) and improved optical quality. However, thermal annealing at the same temperature of a sample of larger QW width (4 nm) did not show QD formation. In this situation, even higher local strains around QWs were speculated. Also, degraded optical quality was observed. © 2003 American Institute of Physics.
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I. INTRODUCTION

Indium-rich cluster formation in InGaN/GaN quantum well (QW) structures results in potential fluctuations and hence the effect of carrier localization (CL).^{1–3} The mechanism of CL has been widely used for interpreting observed optical behaviors in such a compound, such as the S-shaped temperature dependent variation of photoluminescence (PL) spectral peak.^{4,5} On the other hand, the large lattice mismatch between InGaN wells and GaN barriers leads to significant strains in the well layers. The strain-induced piezoelectric field, which generates the quantum confined Stark effect (QCSE), has also been used for explaining measured optical phenomena, such as the excitation power dependence of PL spectral peak.^{6–8} In this effect, electrons and holes are spatially separated. Hence, radiative transition rate is reduced and PL decay time is elongated.^{9,10} It is expected that both effects of CL and QCSE play certain roles in photon emission mechanisms of such a compound structure.

Indium-aggregated structures depend on the nominal indium content of InGaN and the degree of spinodal decomposition.¹¹ They also rely on the strain energy built during the growth of InGaN QW layers. Therefore, the designated QW width becomes a crucial factor in cluster formation and the consequent photon emission characteristics.^{12,13} In InGaN compounds, postgrowth thermal annealing processes for changing cluster structures and their photon emission properties were reported.^{14,15} Formation of regularly embedded InGaN or InN quantum dots (QDs) around the designated well layers was observed upon thermal annealing under an appropriate condition.¹⁵ PL intensity was significantly increased with the formation of regular QD structures.

We report the different thermal annealing results (including photon emission properties and material microstructures) in InGaN/GaN QW structures of different QW widths. Because of different levels of built strain energy in different samples, thermal annealing resulted in different cluster structures and hence quite different optical properties. Continuous PL and time-resolved PL measurements were conducted to show various optical behaviors. High-resolution transmission electron microscopy (HRTEM) images were obtained to demonstrate the variations of microstructures. This article is

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FIG. 1. Variations of PL peak positions vs temperature of the three samples under various thermally annealing conditions.

organized as follows: In Sec. II, the structures of the used samples are described and the optical measurement results are discussed. The HRTEM results are reported in Sec. III. The interpretations of the measurement results are discussed in Sec. IV. Finally, conclusions are drawn in Sec. V.

II. SAMPLE PREPARATION AND OPTICAL MEASUREMENT RESULTS

The samples were grown on *c*-plane sapphire with metalorganic chemical vapor deposition. Following the deposition of 30 nm GaN buffer layer and a 2.3 μm GaN layer, QW structures consisting of five pairs of $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ well and 10-nm-thick GaN barrier were grown. Three samples of different well widths at 2, 3, and 4 nm were prepared and referred to as samples w20, w30, and w40, respectively. The growth temperatures were 1010 and 720 $^{\circ}\text{C}$ for GaN and InGaN, respectively. As-grown samples were thermally annealed in a quartz tube furnace at different temperatures ranging from 800 to 900 $^{\circ}\text{C}$ in nitrogen ambient for 30 min.

PL spectral peak variations with temperature of the three samples under various thermal annealing conditions are shown in Fig. 1. After thermal annealing, the S-shaped variation of PL peak is maintained in each case. Thermal annealing results in blueshifts of PL peak in w20 and redshifts in w30 and w40. Also, in all samples thermal annealing at 800 $^{\circ}\text{C}$ leads to the largest spectral shifts. As thermal annealing temperature increases, the blueshift or redshift is reduced. Figure 2 shows the temperature-dependent variations of integrated PL intensity of the as-grown and annealed samples. The integrated PL intensities were enhanced upon thermal annealing in w20 and w30, particularly significant in w20. However, that of w40 was reduced. From Figs. 1 and 2, it is interesting to note that the trends of PL peak shifts (blue or red) and integrated PL intensity variations (increase or decrease) with annealing temperature are the same in each of the three samples. Thermal annealing at 800 $^{\circ}\text{C}$ always leads to the largest changes. As annealing temperature increases, optical properties generally tend to return to the as-grown condition. However, it is noted that in w20 and w40, the curves of PL peak and integrated PL intensity of 900 $^{\circ}\text{C}$ annealing lie between those of 800 and 850 $^{\circ}\text{C}$ annealing. Nevertheless, in w30 the curves of 850 $^{\circ}\text{C}$ annealing lie between

FIG. 2. Variations of normalized integrated PL intensities vs temperature of the three samples under various thermally annealing conditions.

those of 800 and 900 $^{\circ}\text{C}$ annealing. This difference indicates different dependencies on annealing temperature of various samples.

Figure 3 shows PL decay times at individual PL spectral peaks as functions of temperature in w20 and w30 under different annealing conditions.¹⁶ Thermal annealing results in increases of PL decay times in both samples. In particular, the increases of w20 and w30 occur mainly in the high and low temperature ranges, respectively. The variation trends with annealing temperature of these two samples are the same as those of PL spectral peak and integrated PL intensity, as shown in Figs. 1 and 2. The as-grown sample of w20 manifests a two-peak feature in PL decay time variation with temperature. Thermal annealing particularly enhances the peak of higher temperature. On the other hand, as-grown w30 shows a one-peak feature. The peak was enhanced upon thermal annealing. Figure 3 also shows the PL decay time variation of as-grown w40. After thermal annealing of this sample, the PL decay times become too long to be well calibrated with our measured data.

III. HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY IMAGES

Figures 4(a) and 4(b) show the HRTEM images of as-grown and 800 $^{\circ}\text{C}$ annealing w20. The as-grown w20 shows highly irregular and diffusive cluster structures. Clusters diffuse from the designated QW layers into barriers. After ther-

FIG. 3. Variations of PL decay times vs temperature of w20 and w30 under various thermally annealing conditions. That of the as-grown w40 is also shown.

FIG. 4. HRTEM images of (a) as-grown and (b) 800 °C annealed w20 samples.

mal annealing at 800 °C, cluster structures become much more regular. QDs with sizes of 3–5 nm are quasiregularly arranged in the designated QW layers. A similar HRTEM image was obtained in a sample of a similar structure under thermal annealing.¹⁵ Energy-filter transmission electron microscopy has been used to identify the existence of coupled QDs. To further provide evidence of the QD structure in Fig. 4(b), Fig. 5 shows an atomic-scale HRTEM image of the 800 °C annealed w20 sample with nm-scale energy dispersive x-ray (EDX) spectroscopy results within a QD-like cluster. Note that the contrast distribution in a HRTEM image is expected to change in zooming the microscope. With EDX measurements, the indium compositions at the five locations, indicated with arrows, were estimated to be 54%, 42%, 32%, 28%, and 18% from upper left to lower right. Although EDX measurements cannot give us accurate indium composition, the variation shown in Fig. 5 does provide us with strong evidence of QD structure. Figures 6(a) and 6(b) show the

FIG. 5. An atomic-scale HRTEM image of the 800 °C annealed w20 sample with nm-scale EDX measurements at five locations within a QD (indicated with arrows), corresponding to 54%, 42%, 32%, 28%, and 15% of indium from upper left to lower right.

FIG. 6. HRTEM images of (a) as-grown and (b) 800 °C annealed w40 samples.

HRTEM images of as-grown and 800 °C annealing w40. In the as-grown sample, contrast spots of irregular sizes and shapes can be seen around the designated QW layers. Certain line features are quite clear. Although HRTEM images can be affected by the process procedures of samples, Fig. 6(a) does show quite a different structure from that in Fig. 4(a). High strain energy is expected in w40. It led to quite poor photon emission efficiency. After thermal annealing, the major features in the HRTEM image are similar to those of the as-grown sample, leading to the speculation that strong strains still distribute around the designated QW layers after thermal annealing. The HRTEM image of as-grown w30 is similar to that of as-grown w40. However, after thermal annealing at 800 °C, the HRTEM image looks more like annealed w20. From Fig. 2, it is concluded that the structure shown in Fig. 4(b) is preferred for enhancing photon emission efficiency.

IV. DISCUSSIONS

In w20, upon thermal annealing, spinodal decomposition may dominate the process of relaxing the strain energy built in the well layers. In this process, the “up-hill” diffusion results in the gathering of indium toward their cores and forms the more regular structures in Fig. 4(b).^{11,15} However, in w40 because the larger well width leads to larger strain energy, spinodal decomposition becomes less effective.¹⁷ In this situation, the strain energy might be relaxed through the formation of more stacking faults or local lattice distortions upon thermal annealing. Stacking faults and local distortions were observed in atomic-scale HRTEM images of as-grown and annealed w40 samples. It is speculated that the thermally annealed w40 may have a higher density of such defects. Such defects exist around clusters and are responsible for the significant integrated PL intensity decrease with temperature

near 50 K, as shown in Fig. 2. Note that in the aforementioned relaxation process of w40, the local strain distribution around a QW may be enhanced although the global stress is reduced. Therefore, the reduction of integrated PL intensity of w40 upon thermal annealing can be attributed to the increase of either local strain (reduced radiative transition rate due to the enhanced QCSE) or defect density. Note that the possibly strong QCSE and high density of such defects in as-grown w40 can also explain the monotonically decreasing PL decay time with temperature, as shown in Fig. 3.

The blueshift of PL peak in w20 upon thermal annealing can be attributed to the better quantum confinement. The causes of redshifts in w30 and w40 could be quite complicated. They result from the interplay of indium content gathering (redshift trend), quantum confinement (blueshift trend) and strain-induced QCSE (redshift trend). Based on the microstructure observations, the enhanced QCSE may play the key role here. The increasing trends of integrated PL intensities and PL decay times of w20 upon thermal annealing are consistent. These trends may originate from the mixed effects of the variations of CL and QCSE after thermal annealing. Stronger CL further prevents carriers from nonradiative recombination and hence stronger PL intensities and longer decay times. A weaker QCSE increases radiative transition rate and hence stronger PL intensity. However, it reduces the PL decay times. Because the PL decay times were increased upon thermal annealing, the effect of enhanced CL seems to play the key role in annealed w20 samples. This conclusion is consistent with the well-shaped QDs in annealed w20. It is also consistent with a previous conclusion that CL dominates in optical properties in a thin well sample.¹² Note that in w30 because the redshifts of PL peak are quite large and the increases of integrated PL intensity are relatively smaller upon thermal annealing, the enhanced local strain-induced QCSE may dominate over CL in the annealing effects of this sample.

The significant increase of PL decay times at relatively higher temperatures after thermal annealing of w20 implies that CL became stronger and defects became less effective in carrier consumption. In w30, upon thermal annealing the significant increase of decay time at relatively lower temperatures is attributed to stronger CL and enhanced QCSE. Based on the discussions above, the latter may dominate. The extremely long decay time of w40 after thermal annealing is attributed to the enhanced local strain-induced QCSE and hence reduced radiative efficiency.

V. CONCLUSIONS

In summary, we have shown the dependencies of optical and material properties of thermally annealed InGaN/GaN

QW samples on well width. In each sample of different QW widths, the results of temperature variations of PL spectral peak, integrated PL intensity and PL decay time showed consistent trends in varying annealing temperature. Different variation trends upon thermal annealing in different samples were also consistent with the results of HRTEM images. Generally speaking, thermal annealing at 800 °C of a narrow QW width (2 nm) structure led to regularly distributed QDs and improved optical quality. On the other hand, thermal annealing at 800 °C of a sample of larger QW width (4 nm) did not show QD formation. In this situation, even higher local strains might exist around QWs. Also, its optical quality was degraded.

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