On Indium Segregation in InGaN/GaN Quantum Well Structures

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ABSTRACT

Indium segregation in InGaN is a crucial phenomenon controlling the optical characteristics of such a compound. Its formation is a natural process due to the large lattice mismatch between InN and GaN. In InGaN, indium compositional fluctuations and phase separated InN clusters can be observed, particularly when the nominal indium content is high. In this paper, we report the results of material characterization, including X-ray diffraction, high-resolution transmission electron microscopy, atomic force microscopy, etc., and optical studies, including photo-luminescence (PL) and stimulated emission (SE). In material characterization, we observed clear indium aggregation and phase separation. Such indium composition variations become more prominent as the nominal indium content increases. Disk-shape features with dimensions of a few nm by a few tens nm near the quantum well regions could be clearly seen. Regarding optical studies, the widely observed S-shape PL peak position variations with temperature were observed and from which the localization energy values of the localized states were calibrated. Also, the side-peak feature of PL spectrum was attributed to the phonon-replica transition. Such a transition could become quite prominent in a sample with high nominal indium content. In the stimulated emission study, the most prominent feature observed was the two-peak distribution of SE spectrum. These two peaks were supposed to originate from the recombination of localized and free carriers, respectively.

Keywords: InGaN/GaN quantum well, indium segregation, photoluminescence, stimulated emission

1. INTRODUCTION

There are now strong evidences showing that InGaN alloy inhomogeneities play a key role in high-efficiency emission of nitride based light-emitting diodes grown on sapphire¹⁻³. In many articles, it was proposed that nano-scale indium composition fluctuations, due to indium aggregation or phase separation, acted as quantum dots (QDs) in optical characteristics⁴⁻⁶. In the QDs, carriers are deeply localized and their migration toward non-radiative defects (dislocations) is hindered. Therefore, high luminescence efficiency is expected if the density of QDs is much higher than that of dislocations. Indium compositional fluctuation or QD formation may arise from several mechanisms, including strain induced island formation, spinodal decomposition, composition pulling effect, and surface segregation effect. It is uncertain which mechanism dominates for the formation of the compositional fluctuations. The influences of the size and distribution of QDs on the optical properties of InGaN alloys or InGaN/GaN quantum wells (QWs) are also unclear. In this paper, we present the results of material and optical analyses of several InGaN/GaN multiple quantum well structures. The results of material analyses reveal the structures of indium aggregation and phase separation. The optical analyses demonstrate important optical characteristics, which result from the indium segregation structures. In Section 2 of this paper, we will describe the structure of the used samples. In Section 3, we discuss the results of material analyses. The optical characterization results will be presented in Section 4. Finally, conclusions will be drawn in Section 5.

2. SAMPLE PREPARATION

The samples used in this study were grown in a low-pressure metal-organic chemical vapor deposition reactor. The InGaN/GaN MQW samples consisted of five or ten periods of InGaN wells with 3 nm thickness. The designated indium compositions of the sample were 15, 20, and 25 %. The wells of the samples with five quantum wells and the barriers of the

sample with ten quantum wells were doped with Si. The Si doping concentration was 10^{18} cm^{-3} . The barrier was 7 nm GaN. In each sample, the QW layers were sandwiched between a 1.5 μm GaN buffer layer on a sapphire substrate and a 50 nm GaN cap layer. The growth temperatures were 1050 and 740 $^{\circ}\text{C}$ for GaN and InGa N , respectively.

3. MATERIAL ANALYSES

Material analyses include the measurements of high-resolution transmission-electron microscopy, atomic force microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction. Figure 1 shows the X-ray diffraction result of a sample with ten quantum wells and 20 % nominal indium content (sample I). The GaN peaks, identified as D, are mainly from cap and barrier layers. The other two peaks, A and C, corresponding to indium-rich and indium-poor phases, provide direct evidences of phase separation, which is attributed to spinodal decomposition. The extended distribution between A and C, including the feature B, indicates strong indium compositional fluctuation with broad variations in size, shape, and indium content in the sample. The broadening phenomenon was found more prominent with increasing designated indium content. The extended distribution terminates from the right at around $2\theta = 33$ degrees, corresponding to about 48 % indium composition. This value is more or less the solubility limit of indium in GaN.

Figure 2 shows the high-resolution transmission-electron microscopy picture of another sample with five quantum wells and 15 % nominal indium content (sample II). The variation of contrast in the picture represents the fluctuation of local indium content. Such indium composition fluctuation has been confirmed with EDX microanalysis. In the picture, five QWs can be well identified. Near these QWs, indium rich clusters can be clearly seen. We have observed that a lower nominal indium content led to a better confinement of indium-rich clusters near InGa N QWs. Disk-shaped indium-rich precipitates (or dots) can be seen with a diameter ranging from 5 to 8 nm and a thickness ranging from 2 to 4 nm. From other samples (not shown in this paper), we discovered that a higher nominal indium content led to the increase of indium-rich cluster size. The interfaces between InGa N and GaN became more diffusive and indium-rich aggregates extended more into GaN barriers as the nominal indium content increased. Meanwhile, a higher nominal indium content resulted in more InN clusters (phase separation), as indicated by fringe patterns. From atomic-scale HRTEM pictures (not shown in this paper), we also observed lattice distortions and planar faults in the samples due to lattice mismatch between InN and GaN. In the selected area diffraction patterns of those samples, clear extra spots were also observed, indicating the presence of both phase separation and ordering along the c axis. The density of the aggregates was estimated to be much higher than that of threading dislocation density.

The atomic force microscopy picture on the sample top surface of sample II is shown in Fig. 3. It shows the density of V-shape defects. Each V-shape defect means a threading dislocation below. We observed that the density of V-shape defects increased with increasing nominal indium content. The V-shape defect density was at the order of 10^9 cm^{-2} on all samples. Because a higher misfit strain was built with increasing indium content, more V-shape defects were formed for strain relaxation. Threading dislocations and V-shape defects were also observed with high-resolution transmission electron microscopy. It was observed that the indium-rich InGa N precipitates with diameter range from 5 to 12 nm preferred aggregating near V-shape defects or threading dislocations. It is believed that the stress field created by the dislocations provides the driving force for the migration of indium atoms toward dislocations.

4. OPTICAL ANALYSES

The symbols in Fig. 4 show the photoluminescence spectral peak position variations with temperature for three samples, all with five quantum wells but different nominal indium contents at 15, 20 and 25 % (samples II, III, and IV, respectively). In all samples, we can clearly observe the well-known S-shape variations, which were usually used for explaining the optical effects of indium composition fluctuations. The spectral peak positions of those samples also demonstrated their relative indium contents. A simple but effective formula has been suggested to characterize the S-shape curve, in which the energy of the peak position E_p is expressed as a function of temperature T , described by^{7,8}

$$E_p(T) = E_p(0) - \frac{\alpha T^2}{T + \beta} - \frac{\sigma^2}{k_B T}. \quad (1)$$

Here, $E_p(0)$ is the energy of the peak position when $T \rightarrow 0$, α and β are the parameters characterizing the shrinkage of E_p , which is assumed to follow Varshni's relation of band gap energy [13], and σ is the parameter describing the thermal distribution effect within the localized states. It should be noted that the $-\sigma^2/k_B T$ term in (1) is derived on the assumption of the non-degenerate carrier distribution and the Gaussian-like density of state, associated with the localized states. As a result, (1) is not applicable in the regime of red shift at low temperatures (below 100 K for samples A and B and below 150 K for sample C) due to the strong degeneracy in carrier distribution. Therefore, (1) is used to fit the data points from the turning points between the red and blue shifts towards the high-temperature regime. In Fig. 4, the solid curves represent the fitting

results by using (1). From the fitting, we can obtain the values of $E_p(0)$, α , β , and σ . Keeping the same α and β parameters in Varshni's relation without the contribution of the $-\sigma^2/k_B T$ term in (1), we can reproduce the pure effect of the band gap shrinkage, as shown with the dotted curves in Fig. 4. The energy difference between the measured PL peak position at the lowest temperature and the intercepted point of the dotted curve at 0 K roughly corresponds to the energy difference between the localized and free-carrier states. This energy difference is called as the localization energy. It is 18.3, 34.4, and 36.27 meV for samples II, III, and IV, respectively. A larger nominal indium content leads to higher localization energy that is consistent with the extent of composition fluctuation.

The PL spectra with low energy shoulders at various temperatures of sample IV are shown in Fig. 5. The shoulder of this sample becomes a separate peak near room temperature. The PL spectra were well fitted with three separate Gaussian distributions, as shown with dotted curves in the insets of Fig. 5. In Fig. 6, the first side-peak positions (upper portion) and the differences between the main and first side peaks (lower portion) as functions of temperature are shown. Since the main and first side peaks show S-shape features for all three samples, it strongly indicates that the carriers participating in the two different processes belong to the same states — the localized states. The energy differences ranging from 50 to 110 meV as temperature increases from 12 to 300 K are roughly correspondent with the phonon energy of InN and GaN⁹. Therefore, we conjecture that the first side peak originates from one-phonon-assisted transition and the second side peak comes from the transition involved in two phonons. Only certain energy states are allowed to participate in the transitions corresponding to the first side peak because the momentum of the phonons participating in the phonon-replica transitions is restricted within a certain range. On the other hand, the emission process for the main peak is free from such an energy-state limitation. Therefore, thermal distribution has a different influence on the different processes, and thus the energy difference between them varies with temperature.

The stimulated emission (or amplified spontaneous emission) spectral variations with temperature for samples III and IV are shown in Fig. 7 and 8, respectively. The stimulated emission spectra always emerge from the high-energy side of the photoluminescence spectra. They are narrower than photoluminescence. We can see that the spectral peak position red shifts with temperature due to the phonon effect. It is particularly interesting to see the two-peak feature in Fig. 8, which describes sample IV with the highest nominal indium content. The alternating solid and dashed curves represent the SE results with temperature varied from 13 K through room temperature (RT). For clarity, we label the three peaks as A, B, and C from the long-wavelength side. The 13 K result corresponds to the highest peak A, the very left peak B, and the highest peak C. As temperature rises, the spectral position of peak A is almost unchanged and its intensity decreases. Also, peak B red shifts and becomes stronger with increasing temperature. For comparison, the normalized PL spectra at 13 K (dashed-dotted) and RT (dashed-dotted-dotted) are also plotted. Peak A, which partially overlaps (on the high energy side) with the low-temperature (LT) and RT photoluminescence spectra, is supposed to come from carrier recombination of localized states. Peaks B and C are supposed to originate from free carrier recombination, corresponding to two different quantum well sub-bands. The red shifts of PL peak and peak B with rising temperature are expected due to band-gap shrinkage. However, peak A position moves little with temperature. Meanwhile, one can see the decreasing and increasing trends of peaks A and B intensities, respectively, with temperature. It is believed that as temperature rises, carriers are thermally excited to move away from the localized states and may occupy free-carrier states. This leads to the decreasing trend of localized state recombination and the increasing trend of free-carrier recombination. The almost unchanged spectral position of localized state recombination (peak A) can also be interpreted for the same reason. Although the global band-gap of the material shrinks with temperature, as shown with the photoluminescence spectra, mobile carriers with thermal excitation result in almost the same spectral position for the maximum gain. Besides, the weaker strain at a higher temperature in the five quantum well structure, which leads to a blue shift of band-gap, may contribute to cancel the global band-gap shrinkage¹⁰.

5. CONCLUSIONS

We have discussed the material and optical properties of several InGaN/GaN multiple quantum well structures of different nominal indium contents and quantum well numbers. From the results of X-ray diffraction, transmission electron microscopy, and others, we could clearly observe the structures of indium aggregation and phase separation. Also, from optical characterizations including photoluminescence and stimulated emission, we calibrated the localization energy between the localized states, due to indium compositional fluctuation, and free-carrier states. Meanwhile, the phonon-assisted transition, which is responsible for the side features of photoluminescence spectra, is characterized. Finally, the two-peak feature of stimulated emission from a sample with a high nominal indium content is discussed.

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Fig. 1 X-ray diffraction pattern of sample I.

Fig. 2 TEM picture of sample II.

Fig. 3 AFM picture of sample II.

Fig. 4 PL spectral peak position variations with temperature for samples II, III, and IV.

Fig. 5 PL spectra of sample IV.

Fig. 6 Parameters of side-bump features of samples II, III, and IV.

Fig. 7 SE spectrum of sample III at various temperatures.

Fig. 8 SE spectra of sample IV at various temperatures.