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# Damage-free Structural and Optical Characterization for InGaN/GaN Multi-Quantum Well Epi-Layers†

YOUNG JOON YOON[1,*], MI-YANG KIM[2] and JOON SEOP KWAK[3]

[1]Nano-Convergence Intelligent materials team, Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Republic of Korea
[2]Central R and D center, Samsung Electro-Mechanics Co. Ltd., 314 Suwon, Republic of Korea
[3]Department of Materials Science and Engineering, Sunchon National University, Chonnam 540-742, Republic of Korea

*Corresponding author: Fax: +82 2 3282 7838; E-mail: yjyoon@kicet.re.kr

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The quality of InGaN/GaN multi-quantum wells, especially the uniformity of composition and thickness, can have a strong influence on carrier localization and it will finally determine the probability of radiative recombination and internal quantum efficiency. However, characterizing the structural properties of multi-quantum wells in an atomic level remains a difficult task, because other existing techniques for measurement of ultra-thin layer are limited in spatial resolution and sensitivity. In addition, analytical artifacts frequently occur in the results from electron microscopy caused by irradiation from the high energy incident beam. To overcome the limitations of the analysis of InGaN/GaN multi-quantum wells for light emitting diodes, high-resolution scanning transmission electron microscopy technique was employed. It was possible to measure both the strain field and indium atom distributions in InGaN/GaN multi-quantum wells without the electron damage. In addition, the new formula was employed to describe the temperature dependence of the integrated photoluminescence intensity from the multi-quantum wells to estimate internal quantum efficiency.

**Key Words: InGaN, GaN, High-resolution scanning transmission electron microscopy, Photoluminescence.**

## INTRODUCTION

Competition between radiative and non-radiative recombination processes determines the internal quantum efficiency of III-V system and plays a critical role in the control of total luminous efficiency of an LED device[1,2]. There are two ways to achieve a high internal efficiency LED design. The first is to enhance radiative recombination probability and the second is to decrease non-radiative recombination probability. Actually, an approach to decrease the source of non-radiative recombination seems to be more reasonable because the optimum structure and design of LED devices which increase the probability of radiative recombination have been already developed by applying heterostructures and controlling the doping concentration. However, even though non-radiative recombination can be reduced, it can never be totally eliminated. A crystal at room temperature has some native defects and their concentrations can be never zero.

The uniformity of composition and thickness of InGaN/GaN multi-quantum wells has a strong influence on the carrier localization and it will finally determine the probability of radiative recombination. On the other hand, the inhomogeneity of multi-quantum wells and crystal defects such as dislocation, stacking fault and inversion domain boundary, are main factors of the deterioration of internal quantum efficiency. Real multi-quantum wells exhibit a number of imperfections which result from the interdiffusion and the fluctuation of composition and thickness in the growth procedure[3-5].

Therefore, it is critical to accurately characterize the thickness and composition of InGaN/GaN multi-quantum wells including various defects, to enhance internal quantum efficiency. However, characterizing the structural properties of multi-quantum wells in an atomic level remains a difficult task, because other existing techniques for measurement of ultra-thin layer are limited in spatial resolution and sensitivity. In addition, analytical artifacts can frequently occur in the results from electron microscopy caused by the irradiation of high energy incident beam[4]. In this study, new analytical techniques and interpretation methods for the characterization of structural and optical properties of InGaN/GaN multi-quantum wells will be described using high-resolution scanning transmission electron microscopy (HRSTEM) and photoluminescence with quantitative and qualitative methods, simultaneously.

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## EXPERIMENTAL

GaN epi-layers were grown on (0001)-plane of sapphire substrates by metal organic chemical vapour deposition. The chemical precursors used for gallium, indium and nitrogen are trimethylgallium [TMG, $Ga(CH_3)_3$], trymethylindium [TMIn, $In(CH_3)_3$] and ammonia ($NH_3$), respectively. To understand the relationship between structure and optical properties, the twelve epi-ready samples, which showed different compositions and thicknesses in multi-quantum wells, were prepared under identical conditions of growth temperature and pressure. To control the composition and thickness of InGaN/GaN multi-quantum wells, the flow of TMIn was varied from 70 sccm to 160 sccm and the growth time was controlled from 95 to 155 sec.

The structural properties of multi-quantum wells, such as interface roughness, indium uniformity and strain effect were mainly characterized by transmission electron microscopy (TEM), FEI Tecnai G2 F20 S-Twin (200 kV) system. Especially, a high resolution scanning TEM (HRSTEM) technique was newly introduced to clarify the change in atomic arrangement caused by strain fields, interdiffusion and phase separation. For the TEM sample preparation, *tri*-pod polishing, which makes it possible to prepare a wedge-shaped specimen with a large area, was employed to minimize the damage caused by ion-milling process. Continuous wave photo-luminescence measurements were performed with the 325 nm wavelength of a He-Cd laser to investigate the optical properties of multi-quantum wells. The specimens were placed in a cryostat for temperature-dependent measurements ranging from 10 to 300 K.

## RESULTS AND DISCUSSION

**Structural properties of multi-quantum wells by scanning transmission electron microscopy:** Internal quantum efficiency is defined as the ratio of radiative recombination to total recombination. It means that all radiative and nonradiative processes occurring in the active layer of the actual devices affect internal quantum efficiency. As described above, it is certain that the excessive inhomogeneity of multi-quantum wells and crystal defects decrease internal quantum efficiency. Therefore, it is essential to establish the procedure to check the inhomogeneity of multi-quantum wells by structural characterization method. Nowadays, higher indium concentration into multi-quantum wells is required to achieve a longer wavelength emission for green colour. As the indium concentration is increased, the chemical homogeneity in the InGaN well is decreased due to the poor miscibility between GaN and InN. In addition, it results from the misfit strain-induced defects due to large lattice mismatch between InGaN and GaN. Various TEM techniques have been used to collect experimental evidence for these nanometer-scale changes in InGaN/GaN multi-quantum wells. Crystal defects in GaN, such as dislocation, stacking fault and inversion domain boundary except point defects, have been characterized by conventional TEM technique and high-resolution TEM (HRTEM). Previous workers reported indium-concentration maps of InGaN well layers, using HRTEM and simulation techniques. However, it is difficult to say that the fluctuation of indium in multi-quantum wells is solely due to the distribution of indium in the grown alloy, because indium in InGaN quantum wells is too sensitive to damage by electron beam in the TEM. Fig. 1 shows the atomic arrangement of GaN epi-layer including InGaN/GaN multi-quantum wells obtained by HRTEM mode with the zone axis. HRTEM uses the phase contrast to show lattice fringes and atomic structures unlike the conventional low/medium magnification TEM techniques that employ thickness or diffraction contrast. However, a large fraction of inhomogeneous lattice strain could be generated in the quantum wells within at most a few minutes after exposing of high energy (200 kV) parallel beam in HRTEM mode. In addition, this high resolution image was an indirect method, which shows lattice interference fringes and atomic structures by phase contrast. Therefore, HRTEM is not the best method for investigating the uniformity of indium in multi-quantum wells.

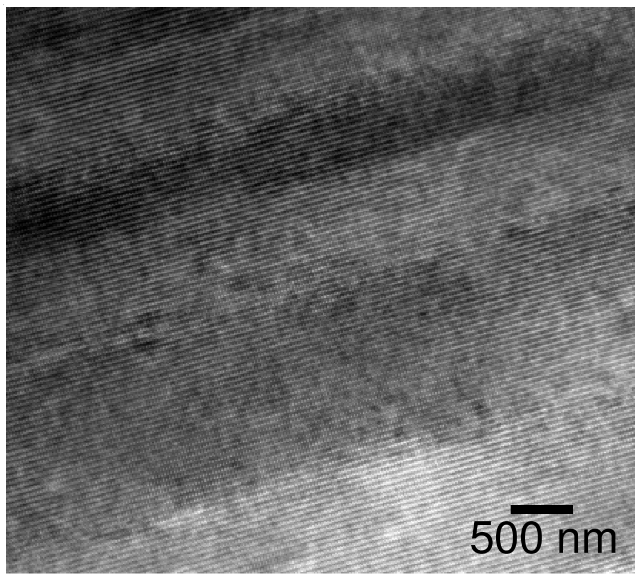


Fig. 1. High resolution transmission electron microscopy (HRTEM) image of InGaN/GaN multi-quantum wells obtained by 200 kV acceleration voltage

Fig. 2(a) and (b) are the HRSTEM images of multi-quantum wells with high-angle annular dark field detector. The uniform InGaN well layer could be seen in Fig. 2 (a) without any interdiffusion of indium using only scanning electron beam. Recently, high-angle annular dark field detector has been used to characterize the atomic structures in the crystals. Compared to conventional TEM, image formation in STEM is somewhat different. In STEM, the electron beam is focused on a small probe (< 0.2 nm) using a special lens system in TEM column and then rapidly scanned in a rectangular pattern across the specimen. Therefore, the fluctuation of indium by electron-beam damage could be decreased sufficiently. The high-angle annular dark field HRSTEM images do not show contrast reversal against thickness and defocus unlike HRTEM, so that bright spots can be considered as real projected atomic columns. The contrast of a high-angle annular dark field STEM image is mainly generated by the Z (atomic number) difference including a small amount of diffraction contrast. The atomic arrangements obtained from HRSTEM are direct images unlike HRTEM, so that the changes of lattice constant and strain could be calculated exactly. As shown in Fig. 2(a), the InGaN well layer is composed of 6 atomic layers and it shows the thickness of 1.679 nm. Considering the c-axis lattice constant of GaN, the increase of lattice constant in InGaN layer, which can be expressed by strain, could be calculated and calculated value for the strain was 0.08.

Before obtaining of Fig. 2(b) in the specific area, HRTEM analysis shown in Fig. 1 had been applied for a few minute and then the inhomogeneous well layer could be observed in the picture. It might be caused by the diffusion of indium when the high electron energy beam was introduced into the specimen in HRTEM mode. In addition, it is possible to estimate the indium non-uniformity in the atomic level using HRSTEM image shown in Fig. 2(b) by counting atomic layer which showed the interdiffusion of indium. Diffusion length of indium could be seen easily in the HRSTEM image by checking the bright contrast in the picture. Compared with Fig. 2(a), indium diffusion was observed through GaN barrier layer and the number of InGaN atomic layer seems to be from 10 to 21.

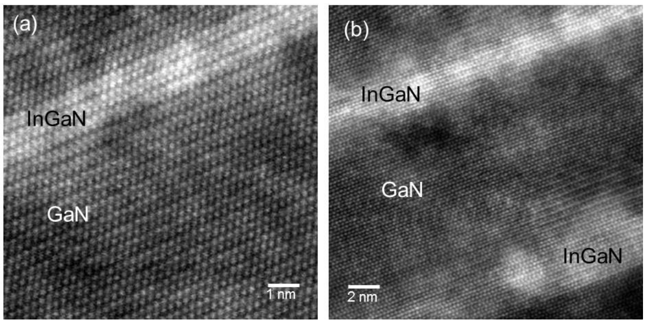


Fig. 2. HRSTEM image of InGaN/GaN multi-quantum wells. (a) HRSTEM image without In damage, (b) HRSTEM image with In interdiffusion after HRTEM analysis

**Optical properties of multi-quantum wells by photoluminescence:** Generally, the analysis of photoluminescence for multi-quantum wells have been widely used for the characterization of optical properties, such as wavelength, emission uniformity and emission power. In this work, to study the internal quantum efficiency and the thermal activation energy associated with the radiative and nonradiative recombination processes, we carried out temperature dependent photoluminescence measurements. As mentioned above, the radiative recombination efficiency of InGaN/GaN multi-quantum wells is surprisingly high in spite of high density of crystal defects caused by large lattice mismatch and thermal expansion coefficient between sapphire substrate and epitaxial GaN layers. This indicates that it is related with strong carrier localization due to the indium clustering in the multi-quantum wells.

The internal quantum efficiency can be estimated to measure the life time decay of carriers in the InGaN/GaN epi-layer system by time-resolved photoluminescence (TRPL)[6,7]. However, it is also estimated by the temperature dependence of the integrated photoluminescence intensity assuming that the internal quantum efficiency is unity at low temperature. To check the dependence of the thickness of InGaN/GaN multi-quantum wells on internal quantum efficiency, three samples were prepared with different well thicknesses (1.3, 1.5 and 1.8 nm). The thickness was measured accurately by HRSTEM analysis, as shown in Fig. 2(a). Fig. 3 shows the temperature dependence of the integrated photoluminescence intensity of three multi-quantum wells samples with different well thickness. The integrated photoluminescence intensity dropped slowly with temperature during low-temperature range, while decreased more rapidly during high-temperature range for the all samples as shown in Fig. 3. This behaviour suggests two nonradiative recombination centers, corresponding to two different activation energies at these temperature regions. In the range of high temperature above 100 K, nonradiative recombination center related to dislocations is the main source for fast decay of photoluminescence intensity.

On the other hand, recombination of carriers captured at the localized potential minima controls slow decay of photoluminescence intensity below the temperature range of 100 K. In means that emission from the InGaN/GaN layers is controlled by two different mechanisms which have different activation energies. Considering these phenomena, the behaviour of the change in photoluminescence intensity with temperature can be expressed by the following formula and each value calculated from Fig. 3 is summarized in Table-1.

$$I = \frac{I_0}{\left[p_1 \cdot \exp\left(-\frac{E_{al}}{k_B T}\right) + p_3 \cdot \exp\left(-\frac{E_{a2}}{k_B T}\right) + 1\right]} \qquad (1)$$

where $E_{a1}$ is activation energy above 100 K, $E_{a2}$ is activation energy below 100 K, $P_1$ is rate constant related to the density of $E_{a1}$ and $P_2$ is rate constant related to the density of $E_{a2}$.

Internal quantum efficiency of multi-quantum wells is strongly influenced by the thickness and the composition of InGaN well layers. Especially, to estimate the internal quantum efficiency of InGaN/GaN system, the ratio of $P_3$ to $P_1$ can be

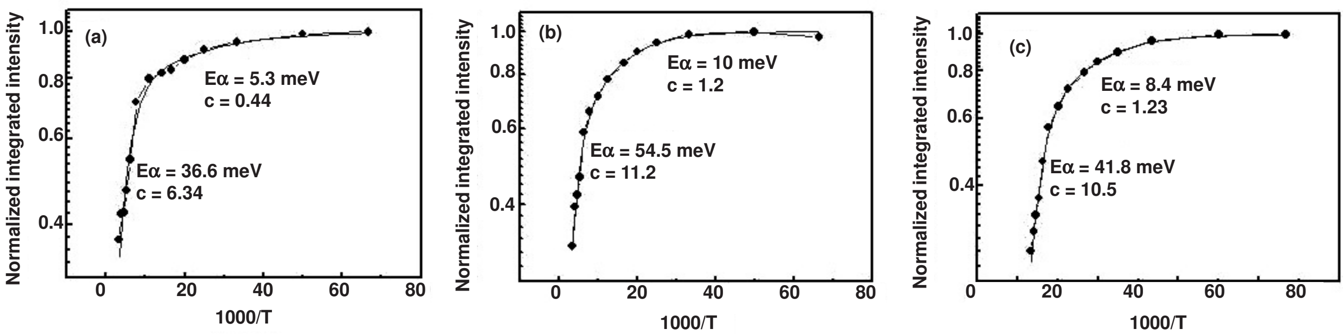


Fig. 3. Temperature dependence of the integrated photoluminescence intensity of multi-quantum wells with the variation of well thickness 1.3 (a), 1.5 (b) and 1.8 nm (c), respectively under the same In concentration in InGaN well layer

TABLE-1
DATA SUMMARY CALCULATED FROM THE GRAPH OF TEMPERATURE DEPENDENCE PL INTENSITY AND FORMULA 1

| Well thickness (nm) | PL wavelength at 300 K (nm) | $P_1$ | $E_{a1}$ | $P_3$ | $E_{a2}$ | $P_3/P_1$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| 1.3 | 419.5 | 6.4 | 36.6 | 0.4 | 5.3 | 0.063 | 0.987 |
| 1.5 | 431.1 | 11.2 | 54.5 | 1.2 | 10.0 | 0.106 | 0.995 |
| 1.8 | 455.6 | 10.5 | 41.8 | 1.23 | 8.4 | 0.117 | 0.998 |

used because it contains the information of radiative and non-radiative recombination, respectively. The calculated value of the $P_3/P_1$ ratio was 0.063, 0.107 and 0.117, respectively. This indicates that the IQE might be slightly increased with increasing thickness of the well layer. These values of P3/P1 ratio and their changes with the thickness variation were very similar to the IQE value obtained from TRPL which is not shown in this paper. It is impossible to measure the IQE value of InGaN/GaN layer with the methods described above, but it can give useful information about the rate of radiative recombination to non-radiative recombination and be applied indirectly to estimate the internal quantum efficiency.

## Conclusion

Through an analysis of high-resolution high-angle annular dark field STEM images, the precise atomic column positions in InGaN/GaN multi-quantum wells as a function of the atomic number contrast (Z contrast) could be elucidated. This resulted in our obtaining useful information for both the strain field and indium atom distributions in InGaN/GaN multi-quantum wells. Compared with conventional HRTEM methods, the damage caused by high energy electron irradiation could be decreased significantly.

To estimate internal quantum efficiency, a new formula was employed to describe the temperature dependence of the integrated photoluminescence intensity from the multi-quantum wells. The fitting conditions and formula was found to be well adapted to the whole samples which were grown under the variation of thickness and composition of InGaN well layers. By using a value of $P_3$ and $P_1$, which express the radiative recombination and non-radiative recombination, respectively, it is possible to estimate the internal quantum efficiency indirectly.

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