Anomalous compositional pulling effect in InGaN/GaN multiple quantum wells

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A series of InGaN/GaN multiple quantum wells (MQWs) was grown by metalorganic chemical vapor deposition with different well thickness. High-resolution x-ray diffraction studies revealed that the In composition is increasing along the growth direction from the bottom to the top of each well layer in these MQWs. While the In composition at the bottom of each well layer almost keeps constant, the increasing rate of In composition becomes obviously larger when the growth temperature is decreased. The important conclusion of this study is that the InGaN/GaN MQWs is shaped like a triangle due to the increasing of In composition from the bottom to the top of the well layer. The emission mechanism of the InGaN/GaN MQWs has to be discussed based on the triangular band gap structure. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1588731]

Although the optoelectronic devices based on the InGaN/GaN multiple quantum wells (MQWs) have been proved extremely successful,[1] the basic property of the InGaN alloy remains a mystery.[2–5] Usually, InGaN alloy or InGaN/GaN MQWs are grown on the GaN templates on sapphire or SiC substrates by metalorganic chemical vapor deposition (MOCVD). Due to large lattice mismatch and high equilibrium vapor pressure, it is very difficult to produce a uniform InGaN film with high quality. The compositional pulling effect, in which the In atoms are excluded from the InGaN film to reduce the deformation energy due to the lattice mismatch during the film growth, was found in the InGaN films grown on the GaN or AlGaN templates.[6,7] As a result, the In composition in the InGaN film increases with the thickness of the film, and it finally constants at a nominal value determined by the thermal equilibrium between the gas phase and the solid phase when the thickness of the film is over the critical thickness. Recently, a detailed analysis on the x-ray reciprocal space mapping (RSM) of the InGaN films shown that both In composition and the extent of relaxation in the InGaN films progressively increase with the film thickness.[8] The InGaN films used in those studies are thicker than 60 nm.[6–8] However, in most of the optoelectronic devices, the InGaN/GaN MQWs are coherently grown on the GaN templates with a well thickness less than 5 nm. If the In composition in the quantum well also increases with thickness as in the bulk InGaN film, its effect on the emission mechanism of the quantum well will be great. In this letter, the In distribution in the InGaN/GaN MQWs grown by MOCVD is investigated by varying the well thickness. It was found that the compositional pulling effect is anomalous in the InGaN MQWs.

MOCVD growth was performed with a Nippon Sanso SR-4000 horizontal reactor by using *C*-plane sapphire as the substrates. Two sets of InGaN/GaN MQWs samples used in this study were grown on 2.5-μm-thick undoped-GaN templates at 745 and 705 °C, respectively. The detailed growth conditions for both GaN templates and InGaN/GaN MQWs can be found elsewhere.[9] There are three samples in each set, which were grown at the same conditions except the growth time for the well. The well numbers and the well growth time were designed to keep the total well thickness constant for the samples in each set. The important growth parameters for all samples are summarized in Table I. The high-resolution x-ray diffractometry (XRD) and asymmetric RSM measurements were carried out on a Philips X'Pert MRDtriple-axis. Diffraction patterns of (004) symmetric reflection were taken by $2\theta/\omega$ scan, and asymmetric RSMs were recorded around (204) reflection. Philips X'Pert Eptaxy was used to simulate the diffraction patterns.

XRD and photoluminescence (PL) techniques are widely used to determine the composition of MQWs consisting of binary and ternary compound semiconductors because of their accuracy and nondestructive character. In the case of InGaN/GaN MQWs, PL is not applicable at the moment because of a lack of the confident band gap of InN and the bowing parameter of InGaN.[4,5] To get the information of InGaN/GaN MQWs from XRD measurements, at least, two satellite peaks would be detectable in a $2\theta/\omega$ scan. The separation between the consecutive satellite peaks of a particular $2\theta/\omega$ scan is determined by the period of the MQWs. The relative positions of the 0 and high order satellite peaks with the GaN peak as the reference, are determined by the average lattice constant of MQWs.[10] The average lattice constant of MQWs is related to the average In composition in the well layer, the well thickness (d_{well}), the barrier thickness ($d_{barrier}$), and the degree of relaxation $R(x)$ via Vegard's law. The degree of relaxation $R(x)$ is defined as $R(x)=[a(x)-a_0(s)]/[a_0(x)+a_0(s)]$, where, $a(x)$ and $a_0(x)$ are the measured and relaxed $\boldsymbol{a}$ lattice constants of InGaN well layer of a given composition, and $a_0(s)$ is the relaxed $\boldsymbol{a}$ lattice constant of GaN. Therefore, in order to get the average In composition in the quantum well layer unambiguously and without any assumption from the simulation of a particular XRD $2\theta/\omega$ scan, $R(x)$, d_{well} and $d_{barrier}$ have to be determined first.

The information about $R(x)$ can be obtained from an asymmetric RSM. Figure 1 is the (204) RSM for the sample

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TABLE I. Growth conditions and XRD results of the InGaN/GaN MQWs investigated in this study.

Sample No.	Growth temperature (°C)	Well No.	Period[a] (nm)	Well (nm)	Barrier (nm)	Average In composition (%)
G186		6	8.1 ± 0.1	1.9 ± 0.22	6.2 ± 0.24	4.5
G187	745	4	9.15 ± 0.2	2.85 ± 0.22	6.3 ± 0.3	6.5
G188		3	10.0 ± 0.1	3.8 ± 0.22	6.2 ± 0.24	8.5
G189		6	8.4 ± 0.1	1.6 ± 0.14	6.8 ± 0.17	6.0
G190	705	4	9.2 ± 0.1	2.4 ± 0.14	6.8 ± 0.17	8.5
G191		3	10.1 ± 0.1	3.2 ± 0.14	6.9 ± 0.17	11.4

[a]Averaged over the results obtained from any two detectable consecutive satellite peaks.

G191; the (204) RSMs for the other samples are similar. The map shows the 0 and ±1 peaks of the MQWs straddling that of the GaN template. All peaks sit on a line parallel to the Q_y axis, indicating that the MQWs are completely coherent to the GaN template. Therefore, $R(x)=0$, for all samples used in this study.

Regarding to the well and the barrier thickness, the calibration process based on the growth of thick (relaxed) InGaN films cannot provide a reasonable estimate for the In composition and the growth rate of an ultrathin layer used in quantum well, even when the same growth conditions are used.[8] From the separation of two consecutive satellite peaks of a high-resolution XRD $2\theta/\omega$ scan, the period ($d_{\text{well}}+d_{\text{barrier}}$) of the MQWs can be deduced. However, it is difficult to get the accurate In composition in the quantum well by simulating the XRD $2\theta/\omega$ scan without the exact well and barrier thickness. We have found that the growth rates for the well and the barrier are different although the same Ga flow rate is used. Therefore, a series of InGaN/GaN MQWs samples was grown at the same conditions with different well growth time. Then, the growth rate of the well layer can be extracted exclusively from the period difference of those samples and the difference between the well growth times, which will give the precise well and barrier thickness.

After getting $R(x)$, d_{well} and d_{barrier}, the average In composition in the quantum well layer can be obtained by simulating a particular XRD $2\theta/\omega$ scan without any other variables. In this study, two sets of InGaN/GaN MQWs, grown at 745 and 705 °C, respectively, have been investigated. The satellite peaks of these MQWs are well resolved and are detectable out to 4th order, indicating that these MQWs are of high quality with sharp interface. As an example, the XRD (004) $2\theta/\omega$ scan of the sample G191 and its simulation are shown in Fig. 2(a). The obtained results are listed in Table I for all samples.

We have determined the average In composition in the quantum well layer of a series InGaN/GaN MQWs grown at the same conditions by varying the well growth time; we also can get the information about the In distribution in the well layer of these MQWs by comparing the obtained results. From Table I, one can find that the average In composition in the well layer of the InGaN/GaN MQWs grown at the same conditions increases linearly with the well width. Because the well layer of these InGaN/GaN MQWs were grown exactly at the same conditions, it is very clear that the In incorporation rate is increasing with growth time during well layer growth, which makes the In composition increasing along the growth direction from the bottom to the top in each well layer. Suppose that it is a linear increase, the In composition in the middle of each well layer should be equal to the average In composition obtained from XRD. From the results of three samples grown at the same conditions, the In compositions at three points can obtained for a set of growth conditions. These points are plotted out in Fig. 3 for the samples grown at 745 and 705 °C. It turns out that these

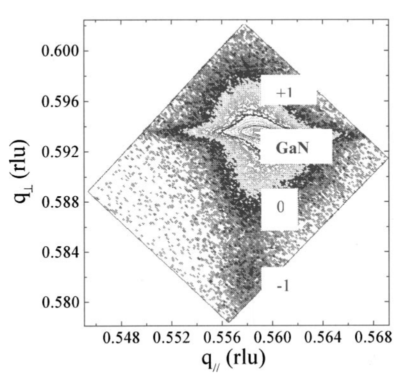

FIG. 1. (204) reciprocal space mapping of sample G191.

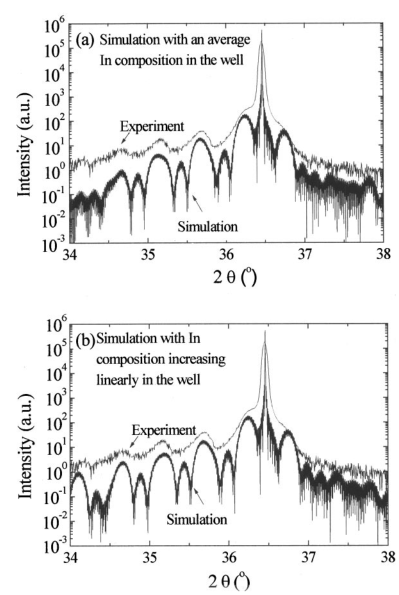

FIG. 2. (a) (004) XRD pattern of the sample 191 obtained with $2\theta/\omega$ scan (upper one) and the simulated pattern (lower one) assuming an In uniform distribution in the well. (b) (004) XRD pattern of the sample 191 obtained with $2\theta/\omega$ scan (upper one) and the simulated pattern (lower one) assuming that the In composition increases linearly from the bottom to the top in the well.

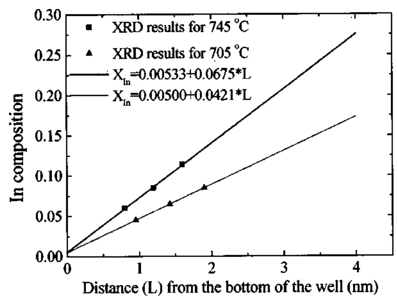

FIG. 3. Position dependence of the In composition in the well layer of InGaN/GaN MQWs grown at 745 and 705 °C, the origin of the X axis is at the bottom of the well layer.

three points are almost on a straight line. The origin of X axis is at the bottom of the well layer. Therefore, the In composition at the bottom of each well layer can be obtained by extrapolating the line to the origin of the X axis. For an InGaN/GaN MQW grown at 745 °C, the In composition at the bottom of each well layer and the increasing rate of In composition is found to be 0.50% and 4.21%/nm, respectively. When the growth temperature is decreased to 705 °C, the In composition at the bottom of each well layer becomes 0.53%, and the increasing rate of In composition increases to 6.75%/nm. While the In composition at the bottom of each well layer almost keeps constant, the increasing rate of In composition becomes obviously larger when the growth temperature is decreased.

The simulation curve in Fig. 2(a) is obtained by assuming a uniform In composition in the well layer. One can find that the overall intensity of the simulation curve decreases faster than that of the experimental one at the low angle side. To make a comparison, the XRD $2\theta/\omega$ scans of these InGaN/GaN MQWs were simulated by dividing each well layer into 100 sublayers and increasing the In composition in these sublayers linearly along the growth direction according to the parameters obtained earlier. Although there was no change in the well and barrier thickness, the overall match between the simulation curves and the experimental ones have been improved greatly, indicating that the assumption of the linear increase of In composition in the well layer is more close to the reality. The simulated curve for the sample G191 are shown in Fig. 2(b) as an example.

The increase of the In composition with the growth time in the well layer of the InGaN/GaN MQWs can be referred to as the compositional pulling effect. The band gap of InGaN will be reduced by the increasing of the In composition. Therefore, the band gap structure of the InGaN/GaN MQWs will be shaped like a triangle by the compositional pulling effect even before considering the quantum confined Stark effect (QCSE), as schematically shown in Fig. 4. The emission mechanism of InGaN/GaN MQWs has to be discussed based on the triangular band gap structure.

Although, there is no report on the compositional pulling effect in the InGaN/GaN MQWs from the other groups, the compositional pulling effect might be quite general in the InGaN/GaN MQWs. A lot of published data strongly suggest that the In composition increases with the well thickness in InGaN/GaN MQWs grown by the other groups.[11] It was reported that the emission energy of compressively strained GaN/$In_{0.08}Ga_{0.92}N$ quantum wells exhibits a strong well width dependence not accounted for by quantum confinement energy shift alone. And it has been explained by QCSE.[11] However, the emission energy of those quantum well samples is much higher than that of thick InGaN epilayer grown at the same conditions after subtracting the quantum confinement shifting. This indicates that the In composition in those quantum well samples is lower than that of thick InGaN epilayer. Furthermore, after subtracting the quantum confinement shifting, the emission energy variation with the well width was modeled by using QCSE in that study. There are totally four experimental points. Two of them are lower than the simulated line by about 50 meV.

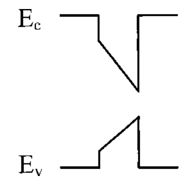

FIG. 4. Schematic view of the band gap structure of InGaN/GaN MQWs with In composition increases linearly from the bottom to the top in the well.

In this study, it is also found that the red shift of the emission wavelength of the InGaN/GaN MQWs with the well width is too large to be accounted for by quantum confinement alone. It is very difficult at the moment to have a quantitative analysis on these data because the confident band gap of InN and the bowing parameter of InGaN are not available.[4,5]

In summary, a series of InGaN/GaN MQWs was grown by MOCVD at the same conditions with different well width. XRD studies on these samples show that the In composition in these MQWs is increasing along the growth direction from the bottom to the top in each well layer. This finding will help to clarify the origin of the emission from the InGaN/GaN MQWs.

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