In-rich $InGaN/GaN$ quantum wells grown by metal-organic chemical vapor deposition

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In-rich InGaN/GaN quantum wells grown by metal-organic chemical vapor deposition

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Growth mechanism of In-rich InGaN/GaN quantum wells (QWs) was investigated. First, we examined the initial stage of InN growth on GaN template considering strain-relieving mechanisms such as defect generation, islanding, and alloy formation at 730 °C. It was found that, instead of formation of InN layer, defective In-rich InGaN layer with thickness fluctuations was formed to relieve large lattice mismatch over 10% between InN and GaN. By introducing growth interruption (GI) before GaN capping at the same temperature, however, atomically flat InGaN/GaN interfaces were observed, and the quality of In-rich InGaN layer was greatly improved. We found that decomposition and mass transport processes during GI in InGaN layer are responsible for this phenomenon. There exists severe decomposition in InGaN layer during GI, and a 1-nm-thick InGaN layer remained after GI due to stronger bond strength near the InGaN/GaN interface. It was observed that the mass transport processes actively occurred during GI in InGaN layer above 730 °C so that defect annihilation in InGaN layer was greatly enhanced. Finally, based on these experimental results, we propose the growth mechanism of In-rich InGaN/GaN QWs using GI. [DOI: 10.1063/1.2173043]

I. INTRODUCTION

Indium nitride (InN) has attracted much attention recently as an important group-III nitride semiconductor.[1–4] Although thermal instability of InN as well as large lattice and thermal mismatches make the growth of high quality InN films extremely difficult,[5] more recent results on InN growth are strongly positive and indicative of potential device applications.[6,7] In this case, InN and In-rich nitrides are important constituents in devices such as light emitting diodes (LEDs), high electron mobility transistors (HEMTs), and solar cells so that the growth of two-dimensional (2D) InN and In-rich nitrides on GaN substrate is inevitable. In our earlier studies,[8,9] we reported the growth of In-rich InGaN/GaN single quantum well (SQW) structures using growth interruption (GI) by metal-organic chemical vapor deposition (MOCVD). During the growth of In-rich InGaN layer, only trimethylindium (TMIn) and ammonia were supplied as precursors, however, the solid-state intermixing of InN with underlying and capping GaN layers occurred during growth, and the actual indium composition in the QW layer was found to be 60%–70% from medium energy ion scattering (MEIS) measurement.[10] And there was the compositional grading of indium at the top and bottom InGaN/GaN interfaces. Based on the indium compositional profile in In-rich InGaN layer, we calculated energy levels and envelope functions by Fourier series method in In-rich InGaN/GaN SQW with compositional grading and we could explain near-ultraviolet (UV) emission observed from the SQW.[10]

We obtained In-rich InGaN/GaN SQWs at relatively high growth temperature, compared with previous reports,[1–4] and at high TMIn flow rate. There existed thickness fluctuations and many structural defects in as-grown InGaN as well as in subsequently grown low temperature (LT)-capped GaN. From photoluminescence (PL) and PL excitation, two different InGaN-related emissions and absorption edges were observed.[11] Cathodoluminescence observation showed that the InGaN layer agglomerated together to form clusters due to the large lattice and thermal mismatches and that the two different InGaN emissions originated from spatially different regions.[11] By introducing GI, however, atomically flat InGaN/GaN heterointerfaces were observed and the InGaN layer thickness reduced to about 1 nm.[8] Moreover, the LT-capped GaN layer had much less defects than the samples grown without GI. Only one InGaN-related emission and absorption edge appeared from the SQW grown with GI. This phenomenon would be related with decomposition and mass transport processes during GI.

In this article, we investigated the initial stage of InN growth on GaN templates and what occurs during GI in InGaN layer to clearly understand the growth mechanism of In-rich InGaN/GaN QW structures using GI. Strain-relieving mechanisms such as defect generation, islanding, and alloy formation were considered to explain the initial stage of InN

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growth on GaN. It was also found that decomposition and mass transport processes actively occurred in InGaN layer during GI. More detailed information will be addressed.

II. EXPERIMENT

In-rich InGaN/GaN QW structures were grown by a MOCVD system equipped with an ammonia preheater. Trimethylgallium (TMGa), TMIn, and ammonia were used as Ga, In, and N sources, respectively. Details of the MOCVD system and the growth procedure and properties of GaN epilayers typically grown in the system were described in our previous reports.[12,13]

The In-rich InGaN/GaN QW samples were grown on (0001) sapphire substrates. The reactor pressure was maintained at 300 Torr throughout the whole process. The InGaN/GaN SQW structures consisted of a 2-μm-thick GaN buffer layer grown at 1080 °C, an InGaN QW layer, and subsequently a 20-nm-thick GaN capping layer grown with or without GI at the same temperature. The typical growth temperature and growth time of In-rich InGaN layer were 730 °C and 90 s, and they varied in the ranges of 710–740 °C and 0–300 s, respectively. GI time was varied from 0 to 10 s. During the growth of In-rich InGaN layer, only TMIn and ammonia were supplied as precursors, and N_2 carrier gas was used. The input TMIn and ammonia flow rate were kept constant at 10 μmol/min and 4 slm, respectively. The In-rich InGaN/GaN multiple quantum well (MQW) structure consisted of a 2-μm-thick GaN buffer layer grown at 1080 °C and four periods of InGaN/GaN MQW layer grown with 0, 3, 6, and 10 s GI at 730 °C. The growth time of all InGaN layers was 90 s. The sequence of GI time in MQW structure was 0, 3, 6, and 10 s from bottom (GaN template) to top layer (LT-capped GaN layer). The GaN barrier thickness was 5 nm and the final GaN capping layer thickness was 20 nm.

Structural properties were examined by atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM). The prepared TEM specimens were examined by a JEOL JEM-3000F microscope operating at 300 kV with a point-to-point resolution of 0.17 nm.

III. RESULTS AND DISCUSSION

A. Initial stage of InN growth on GaN and growth of In-rich InGaN/GaN SQW structure

In our earlier study,[8] we reported the growth of an In-rich InGaN/GaN SQW structure at 730 °C and there existed thickness fluctuations and many structural defects in as-grown InGaN as well as in subsequently grown LT-capped GaN. We found that threading dislocation (TD) density in the SQW was one order of magnitude higher (3×10^9 cm^{-2}) than that of underlying GaN template (2.5×10^8 cm^{-2}). We directly grew a LT-GaN layer on a GaN template at 730 °C to find the origin of increase in TD density in the SQW. Figure 1 shows the surface morphology of LT-GaN directly grown on GaN and the spiral growth mode was observed. The TD density was about 3×10^8 cm^{-2} and it was very similar with that of GaN template. From this, we found that increase in TD density in SQW was originated from the In-rich InGaN layer, not from the LT-capped GaN layer.

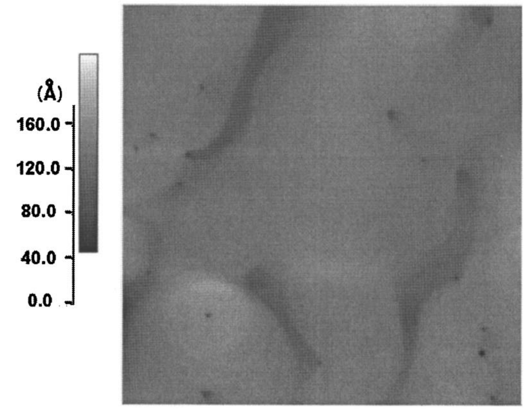

FIG. 1. 2×2 μm^2 AFM image of LT-GaN grown at 730 °C on a GaN template.

Consider InN growth on GaN to find out the origin of increase in TD density in the SQW. The lattice mismatch between InN and GaN is about 11% (Ref. 5), and the critical thickness for misfit dislocation (MD) generation in InN/GaN is indeed less than one bilayer (BL) from Matthews and Blakeslee's criterion.[14] Approximately five BLs (2.5 nm for 90 s growth) of In-rich InGaN formed in the sample would quite exceed the critical thickness and it is not surprising to see the increase in dislocation density for relieving misfit strain. A competing mechanism for relieving strain is islanding.[15] For InN on GaN, however, about 80% of the total strain in epitaxial InN film grown on GaN was initially relieved by defects (dislocations) within first two BLs and further relaxation occurred at a very slow rate and contributed to island formation.[16,17]

To investigate the initial growth mode of InN on GaN template, we changed the InN growth time from 0 to 300 s at a fixed growth temperature of 730 °C. Bare In-rich InGaN surface grown at 730 °C on GaN template showed stepped 2D morphology with the formation of 2D disk-shaped structures on terraces because of the decomposition in InGaN layer during cooling process from our earlier result.[9] Therefore, we introduced LT-GaN capping layer immediately at the same temperature to preserve the InGaN surface. Figure 2 shows the change of TD density as a function of InN growth time. Even in a very short InN growth time (5 s), the TD density was already reached up to the level of 3

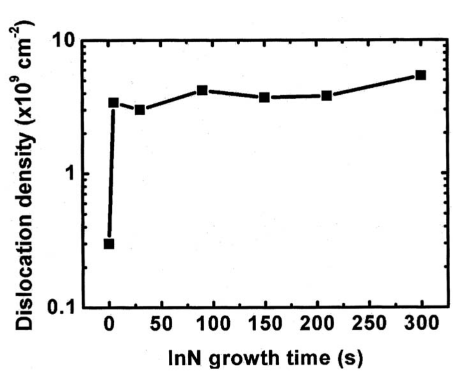

FIG. 2. Change of TD density in In-rich InGaN/GaN SQW grown without GI as a function of InN growth time.

$\times 10^9$ cm^{-2}, and the TD density hardly changed up to 300 s InN growth time. From AFM measurements, we count only the TDs that intersect the top surface, which is only a small fraction of MDs running parallel to the heterointerface.[18]

Thickness fluctuations were found in as-grown InGaN layer by islanding from cross-sectional TEM images.[8] This result is consistent with the observations of Ng *et al.*[16] and Feuillet *et al.*,[17] and theoretical calculation based on Matthews and Blakeslee's model.[14] For the SQWs grown without GI, we believe that the growth rate of InGaN layer was relatively high, so that the atoms had little chances to move laterally to their minimum energy sites. Thus, at the initial stage of In-rich InGaN growth, most of the misfit strain would be relieved by generation of dislocations, and subsequently islanding would diminish the remaining strain. Therefore, as-grown InGaN layer on GaN would have a rough surface with many islands and structural defects. The more detailed discussion including alloy formation to relieve misfit strain will be made in Sec. III C.

B. Decomposition and mass transport processes during GI in InGaN layer

Introduction of GI in In-rich InGaN/GaN SQW was very useful to improve the quality of In-rich InGaN layer and subsequently grown LT-capped GaN layer.[8] After GI, atomically flat InGaN/GaN interfaces were obtained. Furthermore, the InGaN layer had a smooth surface with low structural defect density, and the subsequent GaN layer had a defect density as low as that of the underlying GaN template. We proposed that the decomposition and mass transport processes in InGaN during GI would be responsible for this phenomena.[8]

To confirm this suggestion, we first grew four periods of In-rich InGaN/GaN MQW structure with different GI times. From cross-sectional HRTEM measurement, we found that four periods of InGaN/GaN MQW structure with different GI times were successfully grown, and InGaN layers with GI were flatter and thinner, as shown in Fig. 3. However, InGaN layer was already flattened and thinned to 1 nm at 3 s GI and its thickness was nearly unchanged even at 10 s GI. It was reported that InN has the low dissociation temperature (500 °C,[19] 550 °C,[20] and 630 °C[21]), which possibly depends on nitrogen overpressure. There would be severe decomposition in In-rich InGaN layer due to relatively high growth temperature (730 °C) so that InGaN QW thickness would decrease to 1 nm within 3 s GI. Furthermore, because of the more drastic decomposition in In-rich InGaN at protruded regions during GI, the InGaN surface would be quickly flattened within 3 s GI. From MEIS measurement,[10] we found that there exists a low-indium region near the bottom InGaN/GaN interface. Since the atomic bond strength of GaN is quite larger than that of InN,[22,23] the thermal stability of the In-rich InGaN QW layer was improved when the region near the bottom interface became compositionally graded to the low-indium content InGaN layer with stronger bond, resulting in 1-nm-thick InGaN layer on GaN even after 10 s GI.[24]

By increasing GI time from 0 to 10 s in four periods of MQW, structural properties of In-rich InGaN and LT-capped GaN layers were significantly improved and the integrated PL intensity increased, while the full width at half maximum (FWHM) decreased to 40 meV at 12 K. The PL peak showed a blueshift from 420 to 380 nm by increasing GI time, and more details on optical properties of the MQW can be found in Ref. 25. We believe that GI allows atoms in InGaN layer to have more chances to find their minimum energy sites and dislocations to glide and interact with other dislocations. Therefore, after GI, defects in InGaN layer would be annihilated so that the structural quality of InGaN layer would improved significantly. To verify the mass transport processes in InGaN layer during GI, we varied In-rich InGaN growth temperature in SQW from 710 to 740 °C. The In-rich InGaN growth time and GI time were fixed at 90 and 10 s, respectively. In all samples, the spiral growth mode of LT-capped GaN layer appeared, as shown in Fig. 4, implying that the atomically flat InGaN/GaN interfaces were formed regardless of InGaN growth temperature.[8] To our surprise, despite of a slight increase of InGaN growth temperature from 725 to 730 °C, TD density suddenly decreased from 5

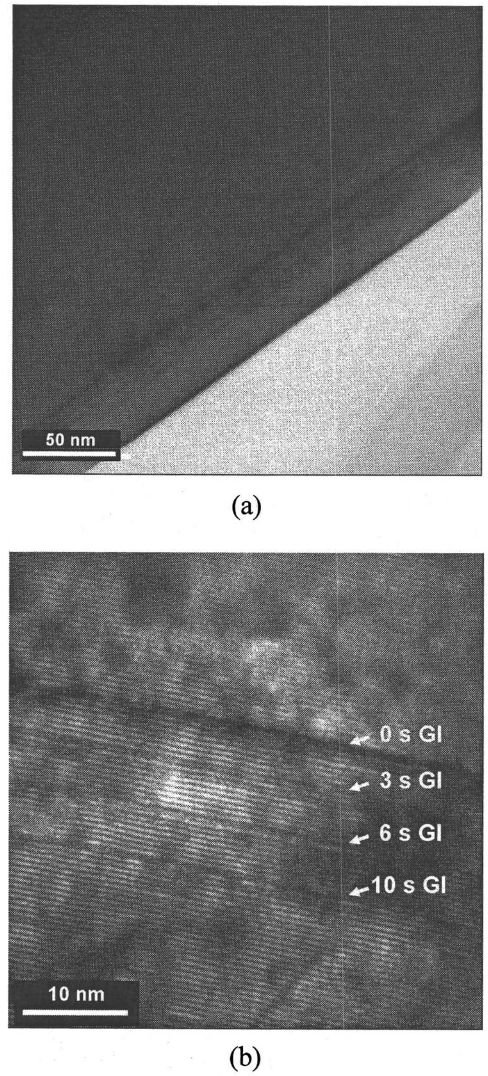

FIG. 3. Cross-sectional TEM image of four periods of In-rich InGaN/GaN MQW structure (a) with 0, 3, 6, and 10 s GI and (b) high resolution image of (a).

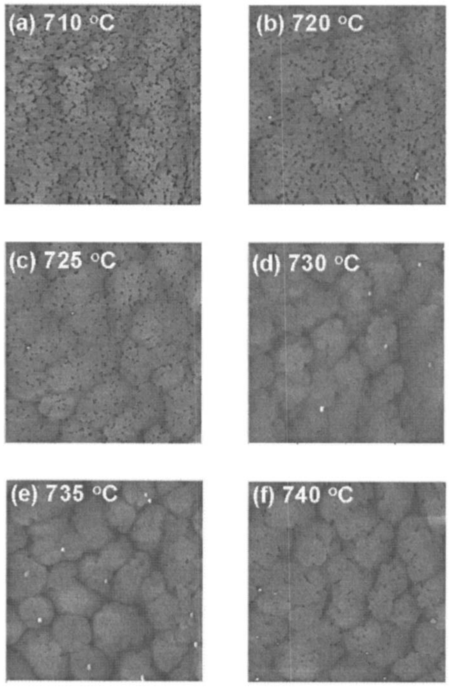

FIG. 4. 4×4 μm^2 AFM images of In-rich InGaN/GaN SQW with 10 s GI grown at (a) 710 °C, (b) 720 °C, (c) 725 °C, (d) 730 °C, (e) 735 °C, and (f) 740 °C.

$\times 10^9$ to 5×10^8 cm^{-2}, as shown in Fig. 5. This means that defect annihilation in InGaN layer was greatly enhanced in this regime. Below 725 °C, decomposition of InGaN layer actively occurred; however, defects generated at the initial stage of InGaN growth still remained after 10 s GI. As a result, 1-nm-thick InGaN layer with high defect density was grown. On the other hand, above 730 °C, both decomposition and defect annihilation in InGaN layer actively occurred so that 1-nm-thick InGaN layer with less defects was formed. The origin of sudden enhancement of defect annihilation between 725 and 730 °C is not clear at this moment, and further study is currently underway.

C. Growth mechanism of high quality In-rich InGaN/GaN SQW structures using GI

We propose a schematic diagram to explain growth mechanism of In-rich InGaN/GaN SQW structure, as shown in Fig. 6. At the initial stage of In-rich InGaN growth, most of misfit strain would be relieved by generation of dislocation and the remaining strain diminished by islanding. Therefore, as-grown InGaN layer on GaN would have a rough surface with many islands and structural defects as shown in Fig. 6(a). Furthermore, InGaN alloying and compositional grading occurred to relieve misfit strain.[10] For heterostructures with large misfit, diffusion and alloy formation are enhanced by the misfit.[26–29] Cowern *et al.* reported an exponential increase in diffusion as a function of strain, indicating a strong dependence of activation energy for interdiffusion on strain.[27] We believe that InGaN alloy formation and compositional grading in InGaN layer would be related with strain-relieving process originated from large lattice mismatch between InN and GaN. More detailed information of indium composition and its distribution in InGaN layer appeared in Ref. 10.

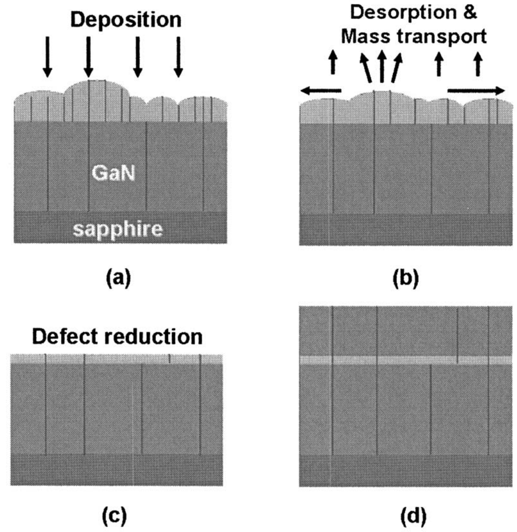

FIG. 6. Schematic diagram of growth mechanism of In-rich InGaN/GaN SQW using GI: (a) during In-rich InGaN growth on GaN template, (b) during GI, (c) after GI, and (d) after LT-GaN capping. The black line in figures indicates the TD.

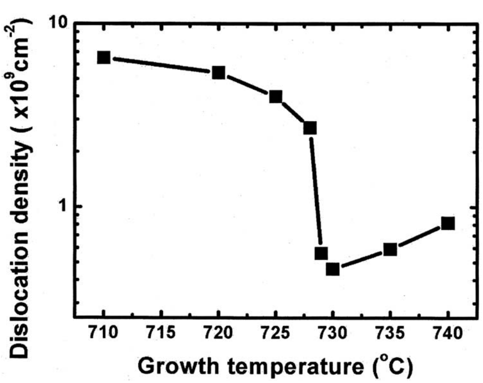

FIG. 5. Change of TD density in In-rich InGaN/GaN SQW grown with 10 s GI as a function of In-rich InGaN growth temperature.

By introducing GI, however, severe decomposition of In-rich InGaN occurred within 3 s due to relatively high growth temperature and the InGaN layer would be further flattened and thinned to 1 nm because of the more drastic decomposition of the In-rich InGaN at protruded regions, as shown in Fig. 6(b). Also, the mass transport processes in InGaN layer actively occurred during GI at 730 °C. Therefore, atoms would have more chances to find their minimum energy sites, and defects in InGaN layer would be annihilated so that the structural quality of InGaN layer improved significantly. As a result, after GI, the InGaN layer would have a smooth surface with low structural defect density [Fig. 6(c)], and subsequent GaN layer would have a defect density as low as that of underlying GaN template as shown in Fig. 6(d).

IV. CONCLUSION

We have studied growth mechanism of In-rich InGaN/GaN QW structures. Initial stage of InN growth on

GaN template was examined, focusing on strain-relieving mechanisms such as defect generation, islanding, and alloy formation. Instead of InN formation, defective In-rich InGaN layer with thickness fluctuations was formed. Introduction of GI before GaN capping made the growth of high quality InGaN layer possible in In-rich InGaN/GaN QW structures. Atomically flat InGaN/GaN interfaces were observed and InGaN layer thickness decreased to 1 nm after GI. We found that decomposition and mass transport processes in InGaN layer are responsible for this phenomenon. Finally, we propose the growth mechanism of In-rich InGaN/GaN QW structures using GI.

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