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Control of the morphology of InGaN/GaN quantum wells grown by metalorganic chemical vapor deposition

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Abstract

Various techniques for morphological evolution of InGaN/GaN multiple quantum well (MQW) structures grown by metalorganic chemical vapor deposition have been evaluated. Atomic force microscopy, photoluminescence (PL) and X-ray diffraction measurements have been used for characterization. It is shown that inclusions, that are generated into the V-defects in the InGaN quantum wells (QW), can be removed by introducing a small amount of hydrogen during the growth of GaN barriers. This hydrogen treatment results in partial loss of indium from the QWs, but smooth surface morphology of the MQW structure and improved optical quality of InGaN wells are obtained. The density of the V-defects could be reduced by reducing the dislocation density of the underlying GaN buffer.

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1. Introduction

Optoelectronic applications for InGaN/GaN quantum well (QW) heterostructures grown by metalorganic chemical vapor deposition (MOCVD) range from the near-UV to the visible spectrum. Fabrication of blue and green light emitting diodes (wavelength range from 450 to 520 nm) requires indium composition of the InGaN layers in excess of 15% [1]. Such a high In content can be achieved by facilitating the In incorporation via lowering the growth temperature to typically below 800 °C and increasing the growth rate to overcome desorption of In. It is also well known that InGaN layers should be grown in nitrogen ambient because the presence of hydrogen (H₂) in the growth environment significantly reduces the incorporation efficiency of In.

Contrary to InGaN, high quality bulk GaN is grown at temperatures in excess of 1000 °C and the surface morphology of GaN grown in H₂ is superior to that of GaN grown in N₂. Thus, the growth regimes for high quality GaN, and for InGaN with high indium content are essentially different. This results in compromises in a process designed for the growth of stacked InGaN wells and GaN barriers. For example, GaN barriers in InGaN/GaN MQW structures are often grown in an N₂ atmosphere at reduced temperature.

When grown under these conditions, the surface of a GaN barrier located on top of an InGaN quantum well layer is characterized by the presence of pits with inclusions located in the center of the pits [2,3] (see Fig. 1). It is believed that the pits, known as V-defects, are formed at the ends of threading dislocations (TDs) [4–9] due to strain induced mechanisms and/or the anisotropy of growth rate of different crystallographic planes within the growing InGaN layer. Inclusions embedded into these V-pits are related to the presence of In rich clusters that have

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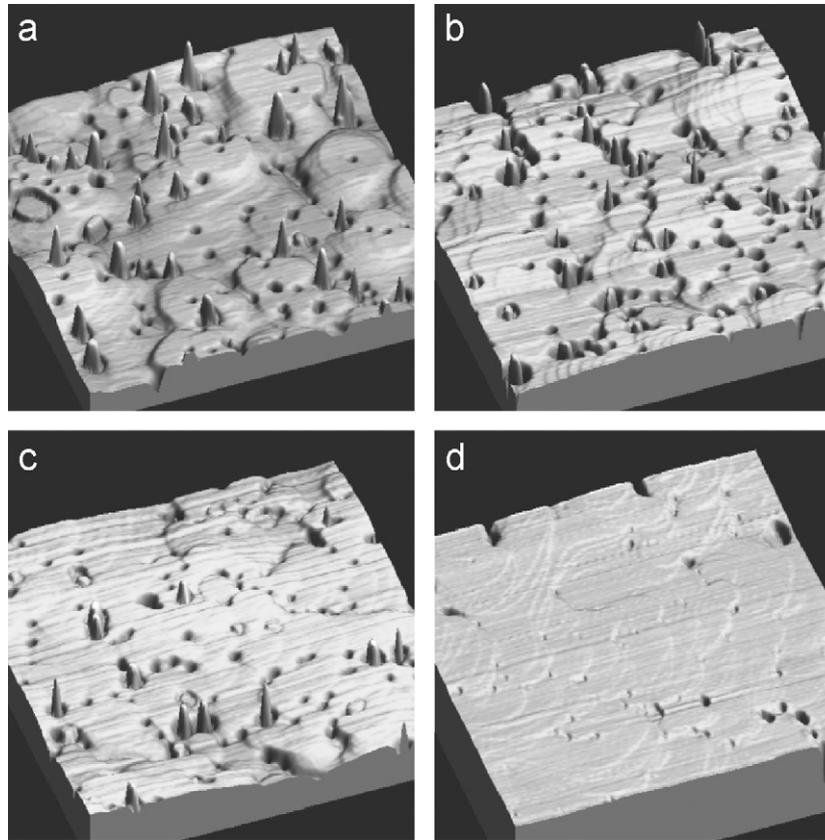


Fig. 1. $3 \times 3 \mu\text{m}^2$ AFM surface scans of the samples: (a) carrier gas for barrier growth: N_2 , $T_{\text{well}} = 745^\circ\text{C}$, $T_{\text{barrier}} = 745^\circ\text{C}$; (b) carrier gas for barrier growth: N_2 , $T_{\text{well}} = 745^\circ\text{C}$, $T_{\text{barrier}} = 900^\circ\text{C}$; (c) carrier gas for barrier growth: N_2 , $T_{\text{well}} = 745^\circ\text{C}$, $T_{\text{barrier}} = 900^\circ\text{C}$, growth interruption 20 s; (d) carrier gas for barrier growth: $\text{H}_2/\text{N}_2 = 0.02$, $T_{\text{well}} = 745^\circ\text{C}$, $T_{\text{barrier}} = 900^\circ\text{C}$. The height scale in all the figures is 20 nm.

nucleated at the point where the TDs intersect the InGaN/GaN interface [10]. These In rich clusters and In rich V-defect side walls are believed to be centers of radiative recombination and to cause photoluminescence (PL) peak broadening to longer wavelengths [7]. Ting et al. proposed that the subsequent low temperature growth of GaN barriers, on top of InGaN, causes 3D nucleation of GaN at the In rich cluster hiding at the apex of the V-pit [10]. During the barrier growth, the inclusions, consisting primarily of GaN, propagate through the barrier leading to unsharp QW/barrier interfaces and non-planar surface of the uppermost GaN barrier layer. This progressively deteriorates the morphology of the successive QWs, which may affect device performance and reliability.

There exists several explanations to the high radiative recombination efficiency of the InGaN/GaN QWs. It is believed that the In rich clusters play a positive role in radiative recombination, since they presumably act as localization centers of carriers in the active InGaN layers and prevent electrons and holes from being trapped into TDs [11,12]. On the other hand, if In rich clusters are located just at the ends of TDs, the assumption about the role of the clusters as centers of radiative recombination is questionable. This is supported by the recent observations by Hangleiter et al. [13]. Their results give strong arguments that the presence of V-defects can result in a

repulsive potential barrier forming around the cores of the dislocations, which causes screening of the dislocations and prevents the carriers of the optically active layer from being trapped by the TDs.

As we have mentioned above, the presence of few nanometers high inclusions, which start growing from the V-pits progressively deteriorate the morphology of the InGaN/GaN QW structures. Therefore, various growth techniques have been employed that strive for smooth planar morphology and sharp interfaces within the InGaN/GaN stack. Growth of barriers at elevated temperature [14], growth of GaN barriers in the presence of hydrogen [10,15] and growth interruption after QW growth [15,16] are believed to be the most efficient approaches for improving the morphology of InGaN/GaN heterostructures. A high growth temperature of the GaN barriers should promote the 2D growth mode and the regrowth of V-defects without the formation of inclusions. Growth interruption and the presence of hydrogen should suppress the density of In rich clusters and thus prevent formation of the inclusions.

In this work, we have studied the dependence of morphological evolution of InGaN/GaN MQW structures on the growth conditions and evaluate the efficiency of each of the approaches mentioned above for morphology improvement. We demonstrate that even a small amount of

hydrogen introduced during the GaN barrier growth eliminates completely the formation of inclusions, whereas growth interruption or barrier growth at elevated temperatures do not have such a strong effect. It is also shown that the elimination of inclusions, which results in a smooth planar interface morphology and a narrow PL linewidth, does not otherwise affect the optical quality of MQW structures, thus questioning the speculated role of the In rich clusters as centers of radiative recombination in InGaN MQWs. We also demonstrate direct correlation between the density of V-pits on the InGaN QWs and the TD density of the GaN buffer.

2. Experimental

The InGaN/GaN MQWs were grown on sapphire substrates by MOCVD system with vertical reactor geometry. Trimethylgallium (TMG), trimethylindium (TMI), and ammonia (NH_3) were used as sources of Ga, In, and N, respectively. The c-plane sapphire substrate was preheated in a H_2 ambient at 1100°C for 300 s, after which a 30 nm thick GaN nucleation layer was grown at 540°C . This was followed by the growth of a 2 μm thick undoped GaN buffer layer at 1050°C . This process results in a GaN buffer with TD density in the excess of $6 \times 10^8 \text{ cm}^{-2}$. The low dislocation density GaN buffer layer in one of the samples was grown with the application of a multistep nucleation layer technique [17], which enables GaN buffer TD density of below 10^8 cm^{-2} to be achieved.

A number of 5-period InGaN/GaN MQW structures were grown on top of the GaN buffer layers at the pressure of 300 Torr. The InGaN layers were grown with TMI/(TMI + TMG) ratio of 0.7 at 745°C with N_2 as a carrier gas. The InGaN layer thicknesses were 3 nm with targeted In composition of 15%. The GaN barrier thicknesses were fixed at 10 nm.

In the reference sample A the GaN barriers were grown at the same temperature and carrier gas composition as the InGaN layers. The effect of increasing the GaN barrier growth temperature was tested in one sample series. In this series the InGaN QWs were first protected by 2 nm thick GaN layer, grown at the same temperature and carrier gas composition as the QWs. Then the temperature was raised and the remaining 8 nm of the barrier was grown at elevated temperature (from 900 to 960°C). The effect of growth interruption was tested by stopping the barrier growth for 5–50 s after the deposition of each 2 nm protective GaN layer and before the deposition of 8 nm GaN barrier at 900°C . The effect of hydrogen was tested in a sample series where the GaN barriers were grown at 900°C and the H_2/N_2 carrier gas flow ratio during the barrier growth was varied between 0.02 and 0.2.

The optical properties of the samples were studied by PL. The PL spectra were measured at room temperature by using a He-Cd laser ($\lambda = 325 \text{ nm}$, power 20 mW) as an excitation source. The surface morphology of the films was imaged with contact-mode atomic force microscopy

(AFM). To evaluate structural parameters and In composition the samples were analyzed with a high-resolution x-ray diffraction (XRD) using $\text{Cu-K}_{\alpha 1}$ radiation.

3. Results and discussions

The morphology of the reference sample A where GaN barriers and InGaN wells were grown at the same temperature is shown in Fig. 1a. As mentioned in the introduction, the surface of the topmost GaN barrier is non-planar and characterized by the presence of V-pits with inclusions located mostly inside the pits. The PL emission measured from the reference sample A is shown in Fig. 2. In addition to the luminescence peak from the InGaN QWs at 480 nm, a long-wavelength shoulder is observed at 500 nm. Full-width half-maximum (FWHM) of the peak is 23 nm. The long-wavelength shoulder is believed to originate either from the In rich clusters located at the apex of the V-defect or from the In rich pyramid sidewalls of the V-defect [7]. The In content of the QWs is 18% as measured by XRD.

Increasing the growth temperature of GaN barriers up to 900°C neither eliminates the pits nor the inclusions, but rather makes the surface outside the pits smoother, as shown in Fig. 1b. This causes a 3 nm blue shift and the removal of the long wavelength shoulder in the PL spectrum (see Fig. 2). The FWHM of the peak remains the same. As the inclusions are unaffected by the elevated growth temperature, we can conclude that the long wavelength shoulder results from the fluctuation of the In content in the QWs or from In rich V-defect sidewalls. Growth of barriers at elevated temperatures removes fluctuations by partial evaporation of In and causes more uniform composition along the QWs. This is further confirmed by XRD measurements that show the decrease

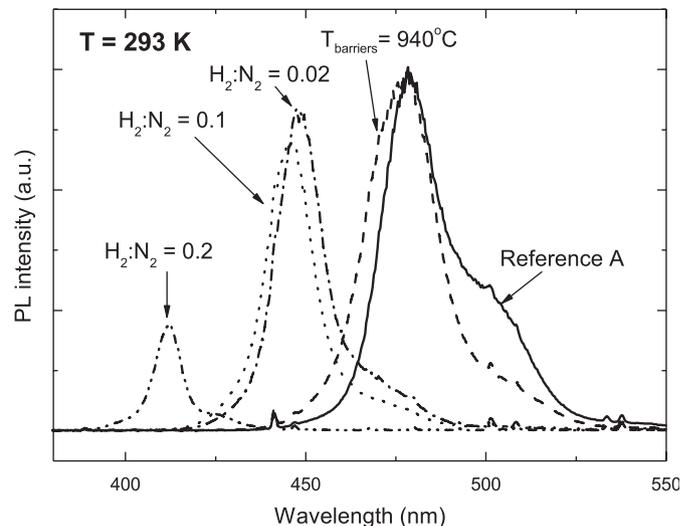


Fig. 2. PL spectra of the samples with different growth procedure of GaN barriers in InGaN/GaN MQW structures: Solid line—reference sample A; dash line—GaN barriers grown at 900°C ; dash-dot line— H_2/N_2 ratio 0.02; dot line— H_2/N_2 ratio 0.1; dash-dot-dot line— H_2/N_2 ratio 0.2.

of average In content from 18 to 15%. The negligible effect of the elevated growth temperature on the surface morphology indicates that the temperature is still too low to achieve complete removal of In rich clusters and planarization of inclusions. Further increase of the barrier growth temperature up to 960 °C results in planar surface with no inclusions. However, high temperature causes severe degradation of InGaN QWs and significant reduction of the PL intensity (spectrum not shown).

To evaluate the effect of the growth interruption (GI) on the MQW structure, we grew a set of samples with GaN barriers grown at 900 °C, with additional GI step of 5 to 50 s after the deposition of each 2 nm GaN cap layer. By increasing the GI time from 5 to 20 s we observed a gradual reduction of the inclusions. An AFM image of the sample with a 20 s GI is shown in Fig. 1c. The number of inclusions, and consequently, the number of In rich clusters is slightly reduced compared to the reference sample A, and the layer morphology is improved. No visible effect on the PL emission spectrum is caused by the growth interruption up to 20 s (spectra not shown). This gives the first indication that In rich clusters may not, after all, act as centers of radiative recombination. Increasing the GI time to 50 s causes degradation of the PL intensity and a 25 nm blue shift compared to the sample with a GI time of 20 s, with no visible change in surface morphology (data not shown). It can be concluded that merely increasing the GaN barrier growth temperature and annealing in situ in nitrogen is not a sufficient method to achieve a good surface morphology.

The effect of hydrogen on the MQW structure was studied in the next set of samples. The GaN barriers of this set were grown at 900 °C and a mixture of N₂ and H₂ was used as a carrier gas during the growth of the barriers. The flow ratio between H₂ and N₂ was varied between 0.02 and 0.2. As can be seen in the AFM image of the surface of the sample grown with H₂/N₂ ratio of 0.02 (Fig. 1d), even this small amount of hydrogen completely eliminates the inclusions and helps to obtain a smooth GaN surface. H₂ is believed to remove the In rich clusters from the QW/barrier interface and thus eliminate the formation of large inclusions on the GaN barrier surface. Along with an improved planar morphology, the presence of 2% of hydrogen in the carrier gas mixture leads to a 30 nm blue shift of the PL peak position (see Fig. 2) and a reduction of the average In content to 10%, as measured by XRD. Simultaneously, we observe narrowing of the main PL peak down to FWHM of 16 nm. The blue shift and the narrowing of FWHM are related to the reduction of the average In content and to the increased compositional uniformity in the quantum wells. Despite the complete elimination of the inclusions and the In rich clusters, the hydrogen treated MQW structure does not show a significant reduction of PL intensity compared to hydrogen free samples.

As can be seen from the AFM surface scan of the sample grown with 2% of H₂ (Fig. 1d), V-defects are left intact.

This can be expected by taking into account that their presence is closely related to TDs. To further confirm this, we grew a similar hydrogen treated MQW structure on top of a low dislocation GaN buffer layer with a TD density below 10⁸ cm⁻², whereas the GaN buffer used for growing rest of the samples had a TD density in the excess of 6 × 10⁸ cm⁻². These dislocation densities were confirmed by directly measuring the etch pit density on the AFM scans of the surfaces of the GaN buffer layers (see Fig. 3a,b). The amount of pits related to V-defects is correlated with the etch pit density and the density is significantly smaller on the surface of the MQW structure grown on the low TD density buffer (see Fig. 3c,d). This data supports previous reports stating that the origin of V-defects corresponds closely to the presence of TDs in InGaN/GaN structures [4–9]. The PL emission measured from the MQW structure grown on a low dislocation density buffer showed no difference, in either intensity or the FWHM of the peak compared to similar structure grown on a buffer with 10 times higher dislocation density (spectra not shown). This, too, suggests that the high radiative efficiency is caused by the self-screening of TD defects [13]. However, generally the recombination mechanism should be determined by competition between radiative recombination in the InGaN well and tunneling through the barriers that screen dislocations. Both of these depend on the In content and, therefore, the situation is different in the case of QWs with lower In content.

Increasing the H₂/N₂ ratio to 0.1 during the growth of GaN barriers does not lead to any noticeable improvements in the morphology compared to the sample grown with H₂/N₂ ratio of 0.02. The PL peak from the sample grown with a H₂/N₂ ratio of 0.1 is blue shifted further only by 3 nm (see Fig. 2) and the XRD measurements show that no further loss of indium takes place. The FWHM of the PL peak remains the same, indicating that also the composition uniformity remains unaffected. When the H₂/N₂ ratio is increased to 0.2 we observe a significant blue shift and a reduction in the PL intensity (see Fig. 2), although no additional loss of In or change in the QW thickness are observed by XRD measurements. This significant blue shift and the reduction of emission efficiency indicates that the increased amount of hydrogen in the growth ambient may deteriorate the overall optical quality of the InGaN layers. This deterioration seems not to be related directly to the loss of In, but to partial relaxation of the InGaN QWs. Relaxation of strain has previously been reported to cause blue shift of PL emission in InGaN MQWs [18]. Formation of 3D clusters on the InGaN surface is most likely governed by relaxation of the elastic energy accumulated in the strained InGaN layer. Elimination of clusters causes strain inside the layer. This strain may further relax via formation of dislocations, which deteriorates the optical quality of the InGaN layer. Further study on this subject is required to understand how defects are generated in hydrogen treated MQW structures.

To further clarify the effect of hydrogen treatment we grew a sample pair with the same In content in the QWs, but one with and one without hydrogen treatment. In this sample pair the In content of the QWs was fixed to 15%, and GaN barriers were grown at 900 °C. During the barrier growth N₂ was used as a carrier gas for the reference sample B, and in the hydrogen treated sample a flow ratio of 0.02 was used for the H₂/N₂ carrier gas mixture. The QW growth temperature of the H₂ treated sample was

reduced by 15 °C to compensate the loss of indium caused by H₂.

AFM surface scans of the sample pair are shown in Fig. 4. It can be seen that there are no inclusions on the H₂ treated sample, while the reference sample B surface is very rough. This indicates that the improved morphology accompanied by the H₂ treatment is caused by elimination of In rich clusters from the InGaN/GaN interface, and not from the reduction of the overall In content of the QWs.

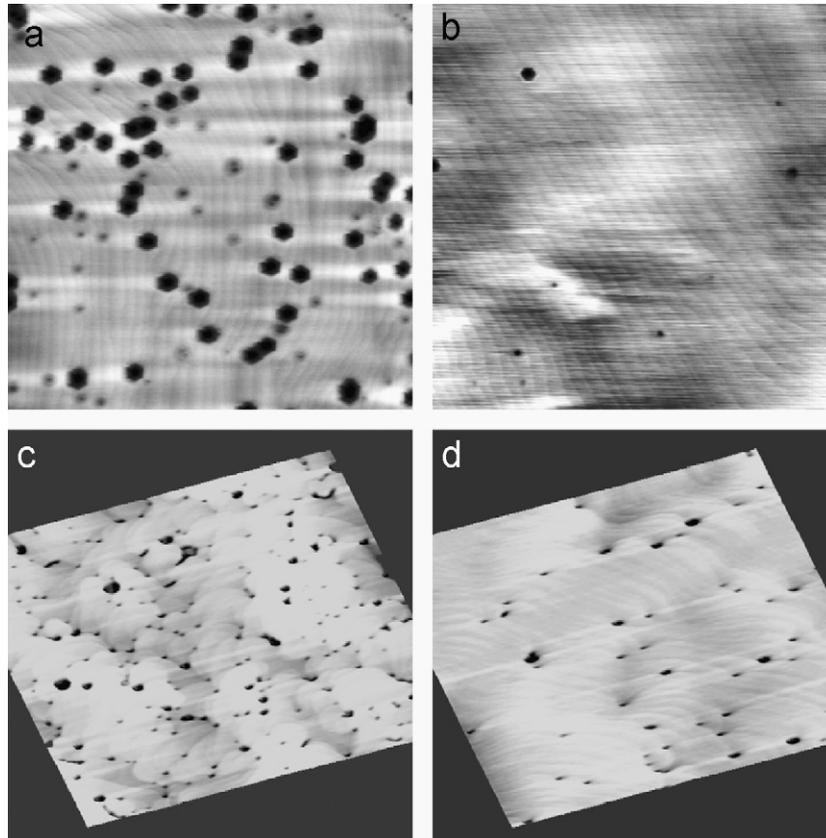


Fig. 3. $5 \times 5 \mu\text{m}^2$ AFM surface scans of the etched surface of GaN buffer layers used for growth of MQW structures with (a) TD density of $6 \times 10^8 \text{ cm}^{-2}$ and (b) below 10^8 cm^{-2} , (c) and (d) surface of hydrogen treated MQW structures grown on these buffers, respectively. The height scale in all the figures is 20 nm.

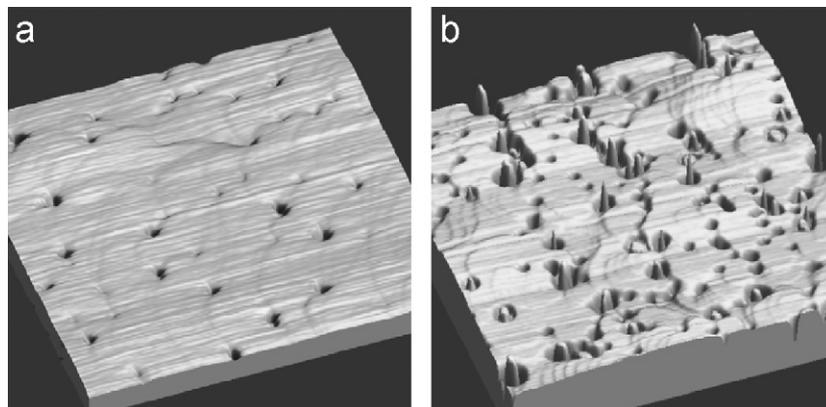


Fig. 4. $3 \times 3 \mu\text{m}^2$ AFM surface scans of MQW samples with 15% In content in the QWs. The GaN barriers were grown with carrier gas flow ratio of: (a) H₂/N₂ = 0.02; (b) H₂/N₂ = 0 (reference B). The height scale in the figures is 20 nm.

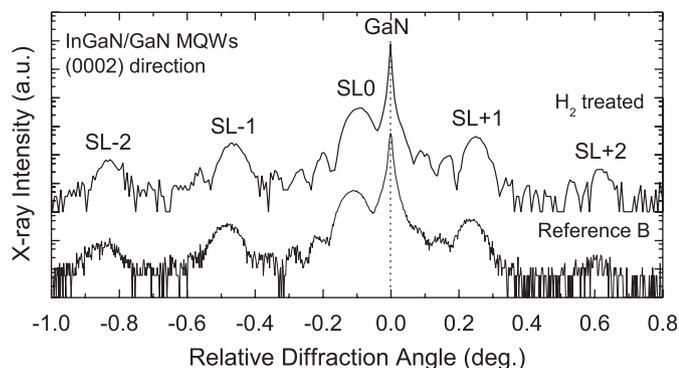


Fig. 5. The (0002) high resolution XRD curves of MQW samples with 15% In content in the QWs. The GaN barriers were grown with carrier gas flow ratio of $H_2/N_2 = 0.02$ (H_2 treated) and $H_2/N_2 = 0$ (reference B).

PL intensity is not affected, but in the H_2 treated sample the FWHM of the PL peak is narrowed from 23 to 18 nm, indicating improved homogeneity of the QWs (spectrum not shown). High resolution XRD $\omega-2\theta$ curves of GaN (0002) reflection of the H_2 treated sample and the reference sample B are shown in Fig. 5. The strongest peaks are from the GaN buffer layers, and both spectra show multiple superlattice (SL) diffraction peaks. In the H_2 treated sample the high order SL peaks are stronger and more pronounced, when compared to spectrum of the reference sample B. This indicates improved layer periodicity and interface quality through the MQW stack.

4. Conclusions

We have studied various growth conditions of InGaN/GaN MQW structures, and their effect on the surface morphology and optical quality. According to our observations, the growth of GaN barriers at an elevated temperature does not lead to any visible improvement of the surface morphology of MQW structure. Additional growth interruption after the growth of InGaN QWs caused a partial reduction of inclusions and an improved morphology, but smooth surface morphology could not be achieved without deteriorating the optical quality of the QWs. High optical quality and smooth surface of the MQW structure was only achieved by introducing a small amount of hydrogen in the carrier gas during the growth of

GaN barriers at an elevated temperature. This resulted in a complete elimination of the inclusions and the related In rich clusters inside the GaN barriers. The hydrogen treatment improved the structural and interface quality of the MQW stack, but also reduced the average In content of the QWs.

It is important to observe that the blue shift of the PL peak and the elimination of In clusters were not accompanied by a change in PL intensity. This allows us to conclude that the In rich clusters do not play a role as centers of radiative recombination of localized excitons, but the high radiative efficiency of InGaN MQW structures results rather from the self-screening of the TD defects. We also demonstrated a clear correlation between the density of V-defects in the MQW structure and the TD density in the GaN buffer. The reduction of TD induced V-pits in the MQW structure did not affect PL intensity, which gives further confirmation of self-screening mechanism of dislocations in InGaN MQWs.

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