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An InGaN/GaN single quantum well improved by surface modification of GaN films

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Abstract

Surface modification of GaN films by *in situ* droplet homoepitaxy of thin GaN layers was employed for improvement of the surface/interface qualities characterized by atomic smoothness, low defect density and surface chemistry being close to stoichiometry. We find that, with surface modification of the GaN films the surface morphology of the subsequently grown InGaN/GaN single quantum well (SQW) was improved with less density of surface pits and indium-rich inclusions. The improvement in surface smoothness and InGaN/GaN surface/interface qualities is desirable for the growth of high-quality multiple QWs (MQWs) structures and fabrication of high-performance and reliable LEDs. PL results show that with surface modification the QW luminescence was significantly enhanced by more than 50% than that without surface modification.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

While InGaN alloys have been successfully applied in fabrication of UV/blue/green and white light-emitting diodes (LEDs) and short-wavelength laser diodes [1–9], the epitaxial growth of high-quality InGaN materials required for high-brightness and reliable device applications, especially for general solid-state lighting applications, is still a major challenge. The epitaxy of layer structures with good control of layer thickness and doping, low threading dislocation (TDs) density and good interface states between wells and barriers has become a prerequisite for commercial applications in high-performance optoelectronic devices. Great efforts have been made to improve the material quality by reduction of pit density, increase of surface/interface qualities and suppressing phase separation/aggregation (when higher indium content is incorporated) [9–17].

During the epitaxial growth, the surface properties (structure, stoichiometry, TDs density, roughness, etc) of GaN films play an important role in the growth behavior (island or step-flow growth, indium incorporation, phase separation/aggregation, strain fluctuation, etc) and optical properties of the subsequent InGaN/GaN quantum wells (QWs) [12–18]. As the indium-rich inclusions and the related V defects would cause loss of interface abruptness and premature thermal degradation and thus reduce the device quality, several techniques have been developed towards suppression of embedded inclusions, e.g. with GaN barrier growth either at an elevated temperature or in the presence of hydrogen [14, 19–22]. In the present work, by surface pretreatment of the GaN films with droplet homoepitaxy for improvement of the surface/interface qualities, we find that, for the InGaN epilayers grown on the surface-modified GaN films, the indium separation/aggregation was suppressed, the surface pit density was reduced and the QW luminescence was strongly enhanced.

2. Experimental methods

The epitaxial growth of GaN templates, InGaN QW and GaN barrier was carried out by metal–organic vapor phase epitaxy

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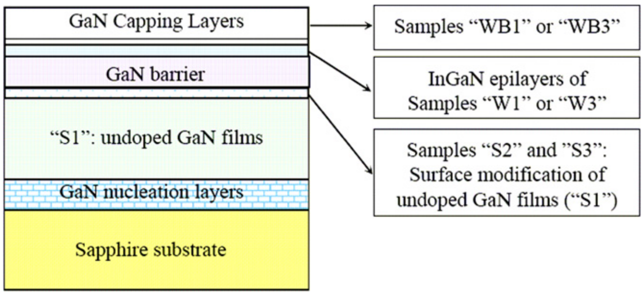

Figure 1. Layer structure for InGaN/GaN SQW on surface-modified GaN films.

(MOVPE) on c-sapphire substrates. The layer structures, preparation procedures and related samples are schematically drawn in figures 1 and 2. Trimethylgallium (TMGa), trimethylindium and high-purity ammonia were used as the source precursors and silane as the n-type dopant.

The preparation of untreated GaN films (sample 'S1') is briefly described below [23]. Firstly the sapphire substrates were cleaned at 1060 °C and 100 Torr for 15 min in H_2 ambient followed by nitridation at 550 °C for 4 min. A conventional 25 nm low-temperature GaN nucleation layer was grown at 535 °C and 500 Torr followed by a high-temperature annealing process. The subsequent growth of $\sim$1.8 μm thick GaN epilayers was carried out at 1035 °C and 100 Torr with $TMGa/NH_3$ ratio gradually increasing from low to high.

The untreated GaN surface was flowed with TMGa in an ambient of H_2 and NH_3 at 500 °C and 500 Torr (sample 'S2') for formation of thin GaN layers on the untreated GaN films. Subsequent high-temperature postannealing at 1050 °C in H_2 ambient resulted in decomposition, desorption and re-evaporation of the newly formed 'soft' GaN layers and formation of Ga droplets on the GaN films. This was followed by droplet homoepitaxy of thin GaN layers by flowing the surface with TMGa and low NH_3 for 800 s at 1035 °C and 300 Torr, where the Ga droplets served as nuclei and self-surfactant (sample 'S3') [24].

The InGaN/GaN SQW was prepared on the untreated and surface-modified GaN films with and without GaN cap layers (samples 'W1', 'W3', 'WB1' and 'WB3'). The growth conditions for the InGaN/GaN QWs remained the same for all the samples. The deposition temperature for the quantum well and the barrier was 742 °C and 827 °C, respectively. Before temperature ramping for the growth of high-temperature barrier layers, a very thin low-temperature GaN layer as a 'well protection layer' was grown at the well temperature for suppressing the indium outdiffusion to the barrier layers. During the growth of the well and barrier nitrogen was used as the carrier gas whereas hydrogen was used as the carrier gas in the other growth stages.

The surface morphologies of GaN and InGaN layers were investigated by an atomic force microscope (AFM, SPA400, Seiko Instruments Inc.). The surface chemical compositions were analyzed by x-ray photoelectron spectroscopy (XPS, PHI Quantum 2000) with an Al Kα x-ray excitation source ($h\nu$ = 1486.6 eV). The photoluminescence (PL) excited by a 325 nm He–Cd laser was measured at room temperature for the GaN and InGaN layers.

3. Results and discussion

Figure 3(a) shows the surface morphology of the untreated GaN films ('S1'). A typical layer structure with an average terrace width of about 130 nm and RMS roughness of 0.19 nm was observed. After flowing the untreated GaN film surface with TMGa in H_2/NH_3 ambient at low temperature (500 °C) and high pressure (500 Torr) for 100 s, drastic changes of surface morphology were observed. As shown in figure 3(b)

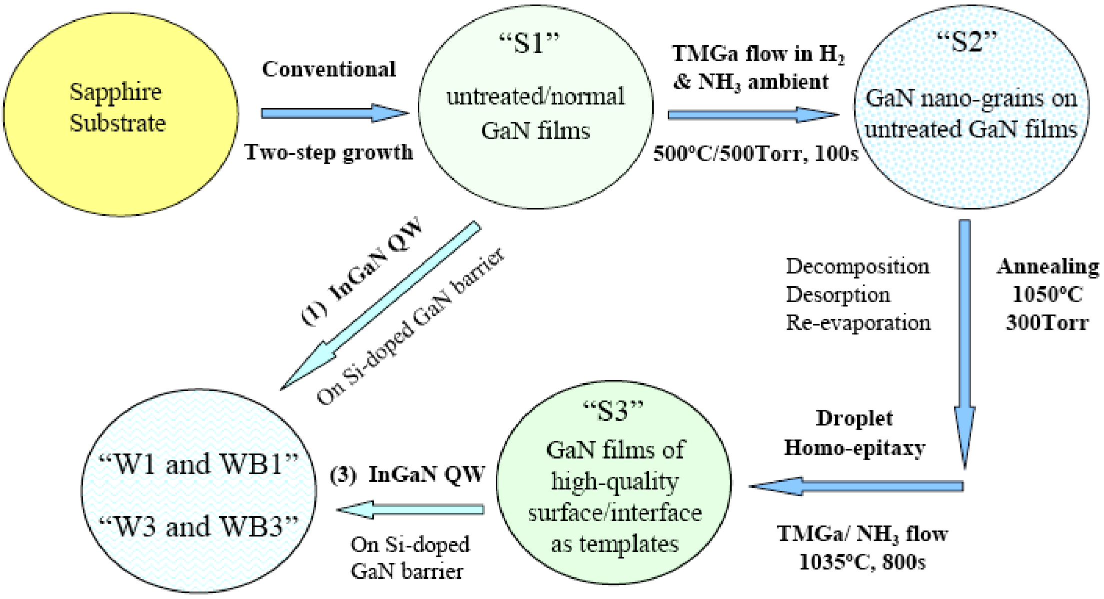

Figure 2. Schematic diagram for the preparation procedures of the InGaN/GaN SQW on treated and untreated GaN films. In the figure, 'S1', 'S2' and 'S3' stand for GaN films at different treatment and growth stages, 'W1' and 'W3' for InGaN epilayers on the untreated and treated GaN films, and 'WB1' and 'WB3' with GaN cap layers on 'W1' and 'W3', respectively.

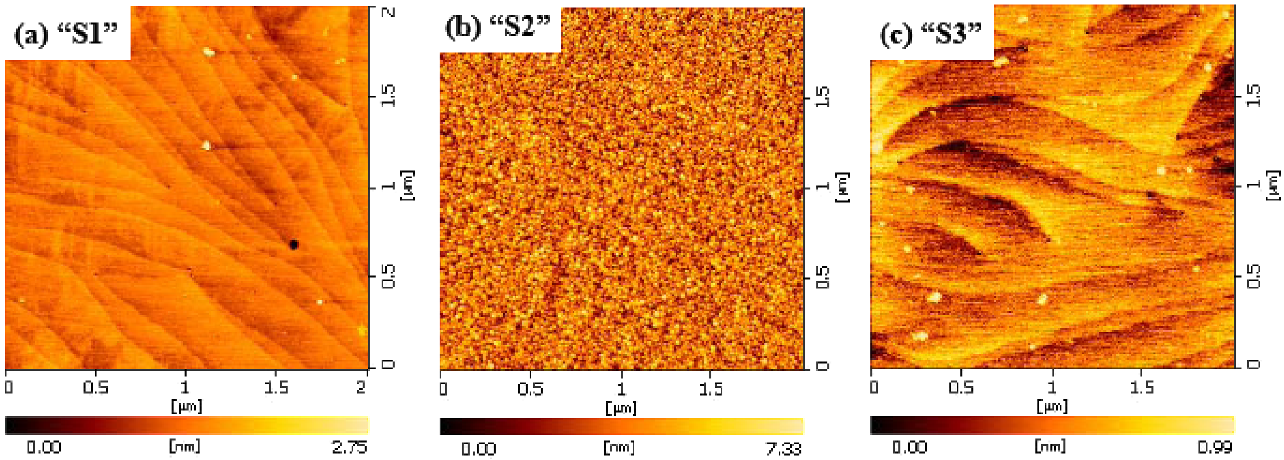

Figure 3. The surface morphology of samples (a) 'S1': untreated GaN films; (b) 'S2': after 100 s TMGa flow over the surface of 'S1' in H_2 and NH_3 ambient at 500 °C and 500 Torr; (c) 'S3': 800 s TMGa flow over the surface of 'S2' in H_2 and low NH_3 ambient at 1035 °C and 300 Torr (GaN droplet homoepitaxy).

for sample 'S2', the surface shows island-like structures with average island size, height, density and RMS roughness of 26 nm, 2.6 nm, 8.5×10^{10} cm^{-2} and 1.0 nm, respectively. After this we performed postannealing of 'S2' at 1050 °C and 300 Torr in H_2 ambient. The GaN nanoislands decomposed, desorbed and evaporated with some small Ga droplets left on the surface. These droplets can serve as the seed nuclei and surfactant for preferential nucleation of newly incorporated GaN. After droplet homoepitaxy of thin GaN layers on the droplet-patterned GaN templates at 1035 °C and 300 Torr with low NH_3 flow rate (sample 'S3'), a very smooth layer-structured surface with RMS roughness of 0.15 nm and terrace width of about 230 nm was observed (see figure 3(c)). The increase of the surface terrace width and smoothness indicates the improvement of surface/interface qualities.

The surface chemistry of GaN films was investigated by measuring the XPS spectra of the Ga 3d5/2 and N 1s photoelectron peaks. Basically, the Ga 3d5/2 photoelectron spectrum can be deconvoluted into three components 1 (19.54 eV), 2 (20.3 eV) and 3 (18.95 eV) corresponding to the chemical bonding of Ga–N (or Ga–ON), Ga–O and Ga–Ga, respectively, whereas the N 1s photoelectron peak can be fitted to three peaks P1 (397.7 eV), P2 (400.7 eV) and P3 (399.0 eV) corresponding to N 1s (N–Ga), N1s (N–O) and N1s (GaON), respectively. The gallium to nitrogen ratio $X^S_{\mathrm{Ga/N}}$ can be estimated from the integrated intensity ratio of the deconvoluted XPS components calibrated by the sensitivity factors. There is $X^S_{\mathrm{Ga/N}} = \frac{(I^1_{\mathrm{Ga3d5/2}}+I^2_{\mathrm{Ga3d5/2}}+I^3_{\mathrm{Ga3d5/2}})/(F_{\mathrm{Ga3d5/2}})}{(I^{P1}_{\mathrm{N1s}}+I^{P3}_{\mathrm{N1s}})/(F_{\mathrm{N1s}})}$, where S denotes the sample name, I the integrated intensity and F the sensitivity factor ($F_{\mathrm{Ga3d5/2}} = 0.438$ and $F_{\mathrm{N1s}} = 0.499$). The intensity of P2 was not included because it was from surface contamination after exposure to air, as described above. We found a different Ga/N ratio $X^{S1}_{\mathrm{Ga/N}} = 0.92$, $X^{S2}_{\mathrm{Ga/N}} = 1.15$ and $X^{S3}_{\mathrm{Ga/N}} = 1.04$ for samples 'S1', 'S2' and 'S3', respectively [24]. This indicates that the untreated GaN films were surface N-rich whereas the surface-modified GaN films were slightly surface Ga-rich. The non-stoichiometry of the GaN surface/interface is usually correlated with native point defects and impurities. For sample 'S1' the presence of N interstitials, Ga vacancies and its complexes such as $(V_{\mathrm{Ga}}O_{\mathrm{N}})^{-3/-2-/-1}$, which is considered to be responsible for the yellow and green luminescence, is likely the origin of formation of the N-rich surface. In the three-step treatment processes, low ammonia flow rate was employed for reduction of NH_3 site blocking of Ga incorporation and thus expected to reduce the formation of Ga vacancies and their complexes [25]. After surface modification, the sample surface/interface becomes more stoichiometric (Ga/N ratio of 1.04), possibly due to lower surface defect density (point defects), especially for the reduction of V_{Ga}-related defects. This is consistent with the following PL results, i.e. significant reduction of defect-related emission (yellow/blue luminescence) by surface modification.

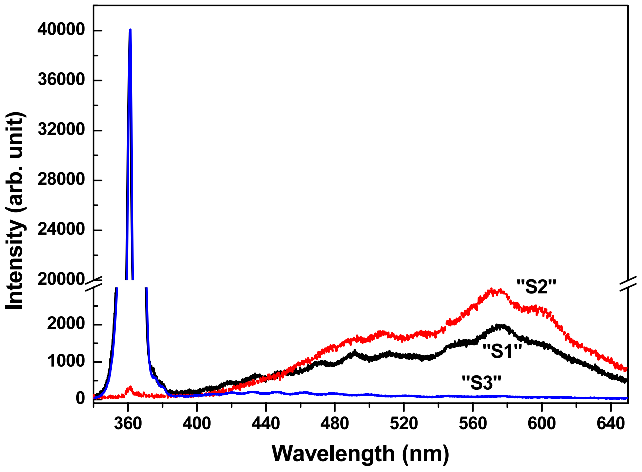

Figure 4. The 300 K PL spectra of GaN films at different treatment stages: 'S1', 'S2' and 'S3'.

As shown in figure 4 the 300 K PL spectra of the untreated and treated GaN films ('S1', 'S2' and 'S3'), three common GaN PL bands, i.e. band-edge emission (BE, 3.432 eV), blue band (BB, centered at 2.8 eV) and yellow band (YB, centered at 2.2 eV), are clearly observed. The full width at half-maximum (FWHM) of the BE emission for the

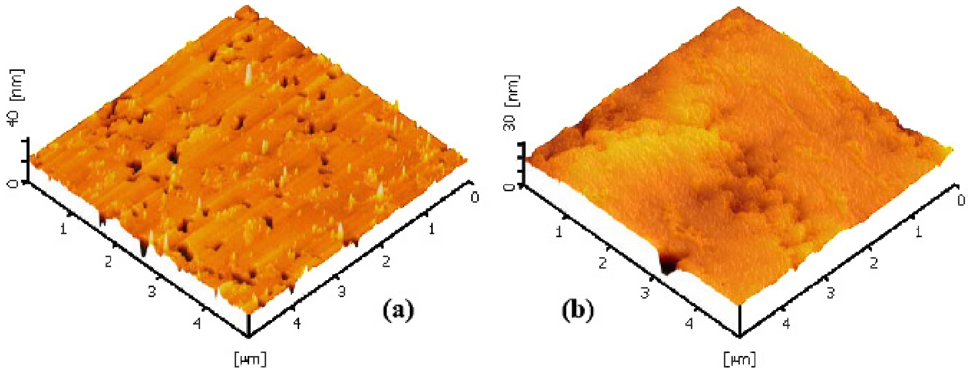

Figure 5. The surface morphology of samples (a) 'W1': InGaN epilayers on 'S1', the untreated GaN films; (b) 'W3': InGaN epilayers on 'S3', the treated GaN films.

untreated GaN sample ('S1') is 34 meV. For sample 'S2' the 300 K PL shows a broadening of the BE with an FWHM of 40 meV and interestingly a strong reduction of the BE intensity. This implied that the BE from the bulk of 'S1' was strongly absorbed by the newly formed non-crystalline GaN nanoislands. On the droplets/nanoislands patterned Ga-rich surface GaN droplet homoepitaxy was carried out at high temperature with low ammonia flow rate ('S3'). Both Ga-rich and high-temperature growth conditions are favorable for the growth of high-quality GaN films (surface/interface) due to the enhanced adatom diffusion [26, 27]. Low ammonia flow rate was employed for elimination of the Ga vacancy and its complexes with O (V_{Ga}–$\mathrm{O_N}$), which is considered as the main source of YB [28]. Significant reduction of the BB (YB) intensity, demonstrating great improvement of the surface/interface qualities, was observed for sample 'S3' by surface modification of GaN films. The improvement of surface/interface qualities is desirable for reliable and high-brightness LEDs.

Figure 5 shows the surface morphology (5 μm × 5 μm) of the uncapped InGaN epilayers on the untreated and treated GaN films ('W1' and 'W3'). As shown in figure 5(a), sample 'W1' on untreated GaN films (i.e. on 'S1') exhibits many surface pits and protrusions without any features of layer structure. The RMS roughness, surface pit and island density is about 2.6 nm, 3.6×10^{8} cm^{-2} and 8.8×10^{8} cm^{-2}, respectively. The surface pits and islands were likely caused by the indium inclusions. These indium inclusions usually originated at the InGaN/GaN interface during the epitaxial growth of InGaN quantum wells on the untreated GaN films. Growth of InGaN at low temperature with indium as antisurfactant would cause the transition of two-dimensional (2D) growth to three-dimensional island growth. Furthermore, the indium-rich inclusions would act as sinks for further indium aggregation and result in a more rough and defective surface. The presence of surface pits and inclusions caused the loss of interface abruptness required for high-performance devices and would also lead to premature thermal degrading during high-temperature processing of LED fabrication, and thus should be suppressed, either by improvement of the InGaN/GaN material quality or by further indium re-evaporation. For sample 'W3' the uncapped InGaN epilayers on surface-modified GaN films (i.e. on 'S3') showed layer structure with much less surface pits. The RMS roughness and surface pit density is about 1.56 nm and 1.6×10^{7} cm^{-2}, respectively. The appearance of layer structure, absence of indium-rich nanoislands and reduction of pit density definitely indicated enhanced 2D growth (suppression of island growth), improved surface smoothness and InGaN/GaN surface/interface qualities, which are highly desirable for the growth of high-quality MQW structures and high-performance LEDs.

Figure 6 shows the XPS spectra (after background subtraction and intensity normalization to the Ga 2p3 peak) of the Ga 2p3 and In 3d photoelectron peaks for samples 'W1' and 'W3'. According to the XPS data book [29], the Ga 2p3 peak is located at 1118.3 eV ($\mathrm{Ga_2O_3}$) and 1117.1 eV (Ga); and the In 3d5 peak is located at 444.8 eV. Slight variation of the peak position was observed due to the changes in chemical environment. The percentage of indium composition can be estimated by $X_{\mathrm{In}} = \frac{I_{\mathrm{In3d5}}/F_{\mathrm{In3d5}}}{(I_{\mathrm{In3d5}}/F_{\mathrm{In3d5}}+I_{\mathrm{Ga2p3}}/F_{\mathrm{Ga2p3}})}$, where I denotes the integrated intensity of the XPS photoelectron peaks and F the sensitivity factors ($F_{\mathrm{Ga2p3}} = 2.751$ and $F_{\mathrm{In3d5}} = 4.53$). As a result we get $X_{\mathrm{In}}^{\mathrm{W1}} \approx 18.0\%$ and $X_{\mathrm{In}}^{\mathrm{W3}} \approx 16.0\%$. As shown above (figure 5), sample 'W1' on untreated GaN films is more rough and defective (surface pits and nanoislands) than sample 'W3' grown on treated GaN films, since indium was more easily incorporated on a rough surface; further, indium-rich nanoislands and surface pits with indium inclusions are also indicative of higher indium content. It is reasonable that higher indium content was observed for 'W1' ($\mathrm{In_{0.18}Ga_{0.82}N}$) compared with that of 'W3' ($\mathrm{In_{0.16}Ga_{0.84}N}$) as estimated by XPS.

Figure 7 shows the 300 K PL spectra of the uncapped InGaN epilayers on the untreated and treated GaN films ('W1' and 'W3'). In addition to the small GaN BE emission peak at 361.5 nm, a strong InGaN QW emission peak at 449 nm for 'W1' and 446 nm for 'W3' was also observed. The peak intensity of the QW emission for 'W3' is about two times that of 'W1', indicating an increase of quantum efficiency by surface modification of the GaN films. Further, taking into account the Fabry–Perot interference effect, the FWHM of the QW emission peak for 'W3' is estimated to be ∼22 nm, which is much narrower than that for 'W1' (∼31 nm). The blueshift of the QW emission for 'W3' compared with that of 'W1'

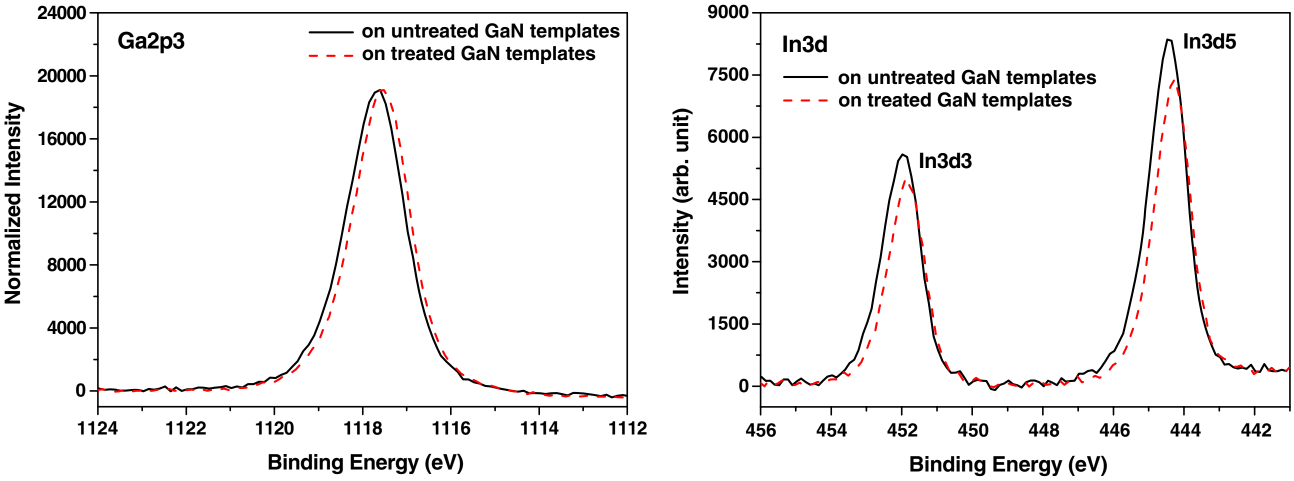

Figure 6. XPS spectra of samples 'W1' and 'W3': (a) the Ga 2p3 photoelectron peak and (b) the In 3d photoelectron peak.

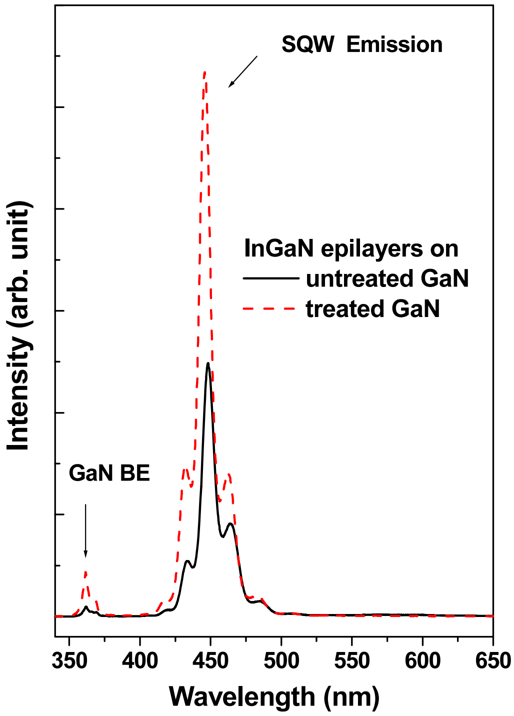

Figure 7. The 300 K PL spectra of samples 'W1' and 'W3'.

is also consistent with the lesser indium content as observed by XPS.

A thin GaN cap layer (∼25 nm) was subsequently grown at 827 °C on the $In_xGa_{1-x}N$ quantum wells. Before temperature ramping for the growth of high-temperature barrier layers, a very thin low-temperature GaN layer as a 'well protection layer' was inserted at the well temperature for suppressing the indium outdiffusion to the barrier layers. With temperature ramping to an elevated temperature the 2D growth of GaN was recovered; further, the indium-rich embedded inclusions and surface pits could be removed or suppressed and thus surface morphology was significantly improved. As shown in figure 8, the surface RMS roughness and pit density for sample 'WB1' is 1.23 nm and 7×10^8 cm^{-2}, respectively. After surface modification of the GaN films, subsequently grown InGaN wells and GaN barriers showed improved surface smoothness (RMS roughness 0.98 nm) and a pit density of 4×10^8 cm^{-2}.

Figure 9 shows the 300 K PL spectra of samples 'WB1' and 'WB3'. As shown in the figure, strong QW emission was observed whereas the GaN BE emission became almost invisible. With surface modification of the GaN films, the QW luminescence for 'WB3' was enhanced by more than 50% compared with that of 'WB1'. Interestingly, in addition to the normal QW emission, a new green emission peak located at about 510 nm was observed if GaN cap layers were grown. As we have described in the experimental section, a thin GaN layer was grown at low temperature prior to the growth of GaN cap layers for suppressing the further outdiffusion of indium components. During the growth of high-temperature GaN cap layers the InGaN decomposition and phase separation/aggregation were enhanced. As a result, an interface layer was formed between the InGaN epilayers and the 'well protection layers'. Such a spontaneously formed interface layer, which was characterized as indium-rich nanostructures [30] and caused by the mechanisms of InGaN decomposition, indium outdiffusion and InGaN phase separation/aggregation of the InGaN QW, is likely responsible for the green emission. Further studies will be addressed for the luminescence mechanism and the formation of indium-rich nanostructures.

4. Conclusion

In situ GaN droplet homoepitaxy was successfully employed for surface modification of GaN films. Features such as improved surface smoothness, surface chemistry close to stoichiometry, and reduced defect-related YB/BB emissions were observed, indicating improvement of the surface/interface qualities. Subsequently the InGaN/GaN SQW was grown on the surface-modified GaN films. We find that the surface quality of the InGaN/GaN SQW on the surface-modified GaN

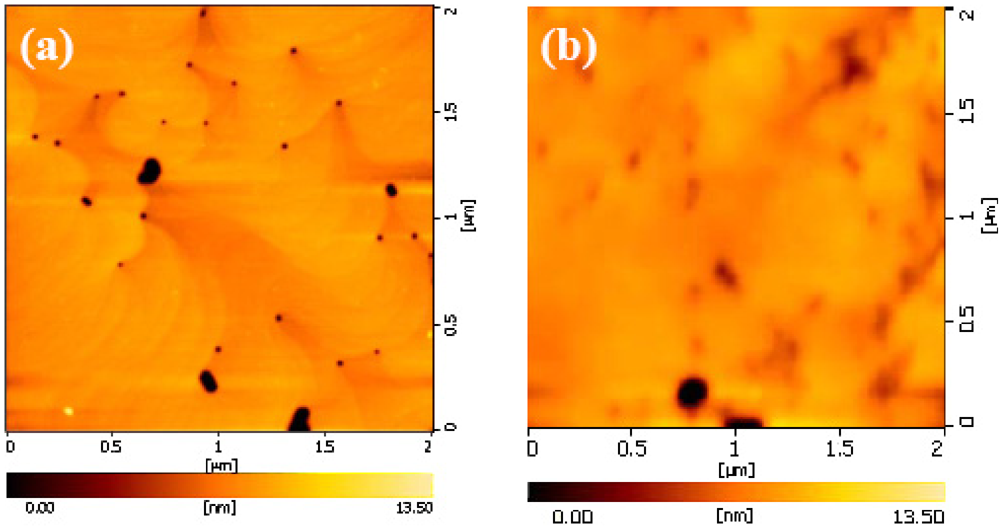

Figure 8. The surface morphology of samples (a) 'WB1': with GaN cap layers on 'W1'; (b) 'WB3': with GaN cap layers on 'W3'.

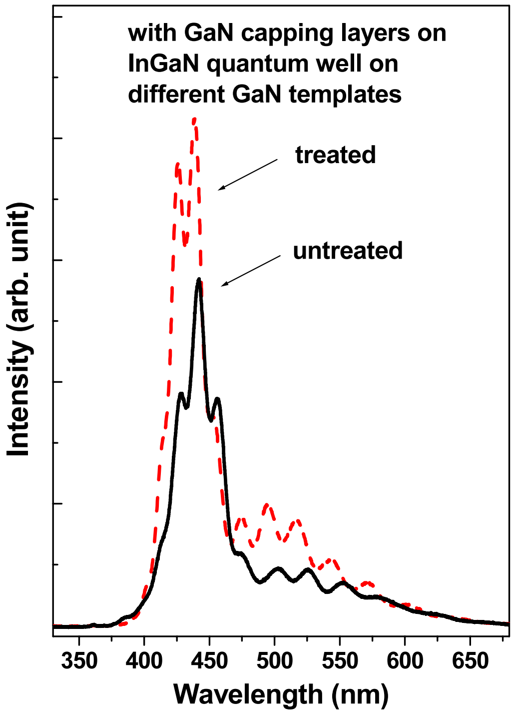

Figure 9. The 300 K PL spectra of samples 'WB1' and 'WB3'.

films was significantly improved with less density of surface pits and indium-rich inclusions. The improvement of surface smoothness and the InGaN/GaN surface/interface qualities is desirable for the growth of high-quality MQW structures and high-performance LEDs. PL results show that, with surface modification, the QW luminescence was enhanced by more than 50% than that without modification.

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