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Surface Modification and Significant Reduction of Yellow/Blue Luminescence of Gallium Nitride

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Conventional undoped gallium nitride (GaN) surface was treated with trimethylgallium (TMGa) flow for 100 s in the ambient of H_2 and low ammonia at 500 °C and 500 Torr followed by thermal annealing at 1050 °C. On the Gallium droplets and GaN nanoislands patterned layer-structured surface, droplet homoepitaxy of thin GaN layers was realized by flowing the surface with TMGa and low ammonia at 1035 °C for 400 s in the ambient of H_2. By such an in situ three-step surface modification, the surface stoichiometry (Ga/N) changed from nonstoichiometry (N-rich, 0.92) to close-to-stoichiometry (slightly Ga-rich, 1.04) with very thin nanoislands (20 nm in diameter and 1 nm in height) patterning on the smooth layer-structured surface. Photoluminescence studies show significant reduction of yellow/blue emissions, which suggests improvement of surface/interface qualities of GaN films.

I. Introduction

The epitaxial growth of III-nitrides usually induces high density of threading dislocations (TDs) and point defects typically on the order of 10^9-10^{11} cm^{-2} and $10^{16}-10^{19}$ cm^{-3}, respectively. The presence of native and extended structural defects (V_{Ga}, V_N, Ga_I, dislocations, domains, etc.) and impurities (C, O, Si, etc.) is detrimental to the performance of electronic and optoelectronic devices. For example, parasitic defect-related emission (yellow/blue/green luminescence and the donor−acceptor pair emission) caused by the electronic states of the point defects, impurities and their complexes,[1−3] and nonirradiative recombination at TDs[4−7] can significantly reduce the luminescence efficiency, operation lifetime, and reliability of optoelectronic devices. While the origin and luminescence properties of extended and point defects have been widely and intensively studied,[1−12] some results still remain controversial, especially for the origin of yellow luminescence.[2,3]

Recently, much effort has been made to reduce the defect density and defect-related emission.[13−18] With the development in miniaturization of high-performance semiconductor devices,[19−23] the quality of surface/interface becomes increasingly important in device performance.[24−27] Surface treatment has been used to modify the growth behavior and properties of GaN-based materials,[16,17,28−30] and enhance the device performance.[25−27,31,32] In this paper we investigated surface modification of GaN films by in situ droplet homoepitaxy of thin GaN layers. Significant reduction of yellow/blue luminescence and change of surface chemistry and morphology were observed.

II. Surface Modification Processes and Investigation Techniques

The epitaxy and in situ surface treatment of GaN films were carried out in a Thomas Swan metalorganic chemical vapor deposition system. The surface treatment procedures and the related samples (name) are schematically depicted in Figure 1. The preparation of untreated GaN films (sample "A") is briefly described below. First c-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 high-temperature GaN epilayers was carried out at 1035 °C and 100 Torr, using trimethylgallium (TMGa) and high-purity ammonia as the source precursors and hydrogen as the carrier gas. The untreated GaN surface was flowed with TMGa in the ambient of H_2 and NH_3 at 500 °C and 500 Torr (stage "I", sample "B") followed by thermal annealing at 1050 °C in H_2 ambient (stage "II", sample "C"). By high-temperature postannealing the newly low temperature deposited GaN layers are expected to decompose, desorb, and re-evaporate on the GaN templates.[33] On the treated surface we performed droplet homoepitaxy[34] of thin GaN layers for 400 s

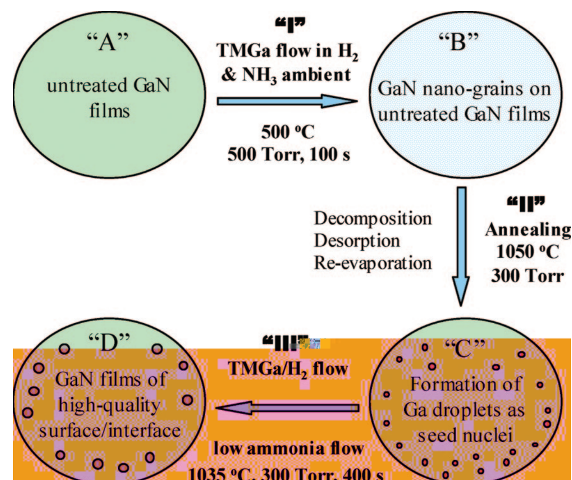

Figure 1. Schematic diagram showing the surface modification processes of GaN films. In the figure, "A", "B", "C", and "D" stand for samples at different growth stages.

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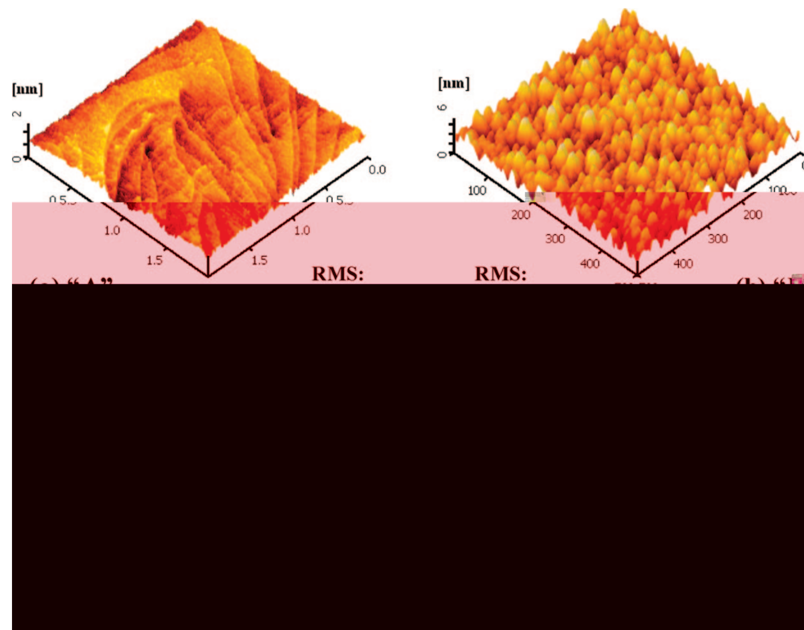

Figure 2. The surface morphology of (a) “A”: untreated GaN films; (b) “B”: after 100 s TMGa flow over the surface of “A” in H_2 and NH_3 ambient at 500 °C and 500 Torr (stage “I”); (c) “C”: high-temperature annealing of “B” (stage “II”); and (d) “D”: 400 s TMGa flow over the surface of “C” in H_2 and low NH_3 ambient at 1035 °C and 300 Torr (stage “III”, GaN droplet homoepitaxy).

at 1035 °C and 300 Torr with low ammonia flow rates (stage “III”, sample “D”).

The surface morphologies of the GaN samples (from sample “A” to “D”) were investigated by atomic force microscope (AFM, SPA400, Seiko Instruments Inc.). The surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantum2000) 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 for different GaN samples at room temperature (300 K).

III. Results and Discussion

a. The Surface Morphologies. Figure 2a shows the surface morphology of untreated GaN films (sample “A”). Typical layer structure with a rms roughness of 0.18 nm was observed. After flowing the untreated GaN film surface with TMGa in H_2/NH_3 ambient at low temperature and high pressure (stage “I”), drastic changes of surface morphology were observed. As shown in Figure 2b for sample “B”, the surface shows islandlike structure with an 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. At stage “II” we performed postannealing of sample “B” at 1050 °C and 300 Torr in H_2 ambient. The GaN nanoislands likely decomposed, desorbed, and evaporated with some small Ga droplets or GaN nanoislands left on the surface (sample “C”). As shown in Figure 2c, the droplet/island size, height, density, and roughness are about 12 nm, 0.3 nm, 1.5×10^{10} cm^{-2}, and 0.15 nm, respectively. These droplets can serve as the seed nuclei for preferential nucleation of newly incorporated GaN. At stage “III” droplet homoepitaxy of thin GaN layers on the droplets/nanoislands patterned GaN template was carried out at 1035 °C and 300 Torr with low NH_3 flow rate (sample “D”). A smooth layer-structured surface of distinct nanoislands on top with increased island size and lower island density was observed as shown in Figure 2d. The nanoislands are of average island size, height, density, and rms roughness of 20 nm, 1.0 nm, 5.6×10^9 cm^{-2}, and 0.16 nm, respectively. This has indicated the coarsening and decay of initial seed nuclei formed at sample “C”.

b. Modifications in Surface Chemistry. The surface chemistry of GaN films (“A”, “B”, “C”, and “D”) has been investigated by XPS. In the XPS experiments all the XPS spectra were referenced to the XPS data book[35] and the C1s peak of fixed peak position at 284.8 eV. The XPS spectra of the Ga3d5/2 and N1s photoelectron peaks are shown in Figure 3. Basically, the Ga3d5/2 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 (see Figure 3, parts a−d). Slight variation of the peak position was observed due to the changes in chemical environment. In the XPS spectrum of N1s photoelectron peak (Figure 3e,f,g,h) strong Ga Auger signals were also observed. As shown in Figure 3e, besides the Ga Auger signals, another two peaks P1 (397.7 eV) and P2 (400.7 eV), corresponding to N1s (N−Ga) and N1s (N−O), respectively, were also included. The chemical component N1s (N−O) was from surface contamination after exposure to air, where nitrogen did not have chemical bonding with gallium atoms, and could be easily removed by sputtering a few nanometers of the surface layer. For “C” and “D” the chemical components (Figure 3g,h) were the same as that of “A” if disregarding the variation in intensity of different components. A new peak P3 (399.0 eV) corresponding to N1s (GaON) was observed for “B” (Figure 3f), which suggested that oxygen was more easily incorporated into GaN to form GaON at low temperature and high pressure compared with that grown at high temperature. This becomes reasonable if we consider the nanoislands-patterned surface morphology, which was rich with dangling bonds easily capturing contaminated oxygen. In comparison, oxygen is more likely to be removed by reaction with hydrogen in H_2 ambient and at high temperature.

The gallium-to-nitrogen ratio (Ga/N) can be estimated from the integrated intensity ratio of the deconvoluted XPS components calibrated by the sensitivity factors. Here we define $X_{Ga/N}^{S} = [(I^{1}_{Ga3d5/2} + I^{2}_{Ga3d5/2} + I^{3}_{Ga3d5/2})/(F_{Ga3d5/2})]/[(I^{P1}_{N1s} + I^{P3}_{N1s})/(F_{N1s})]$ as an estimation of the surface Ga/N ratio, where S denotes the sample name, I the integrated intensity, and F the sensitivity factor ($F_{Ga3d5/2} = 0.438$ and $F_{N1s} = 0.499$). The

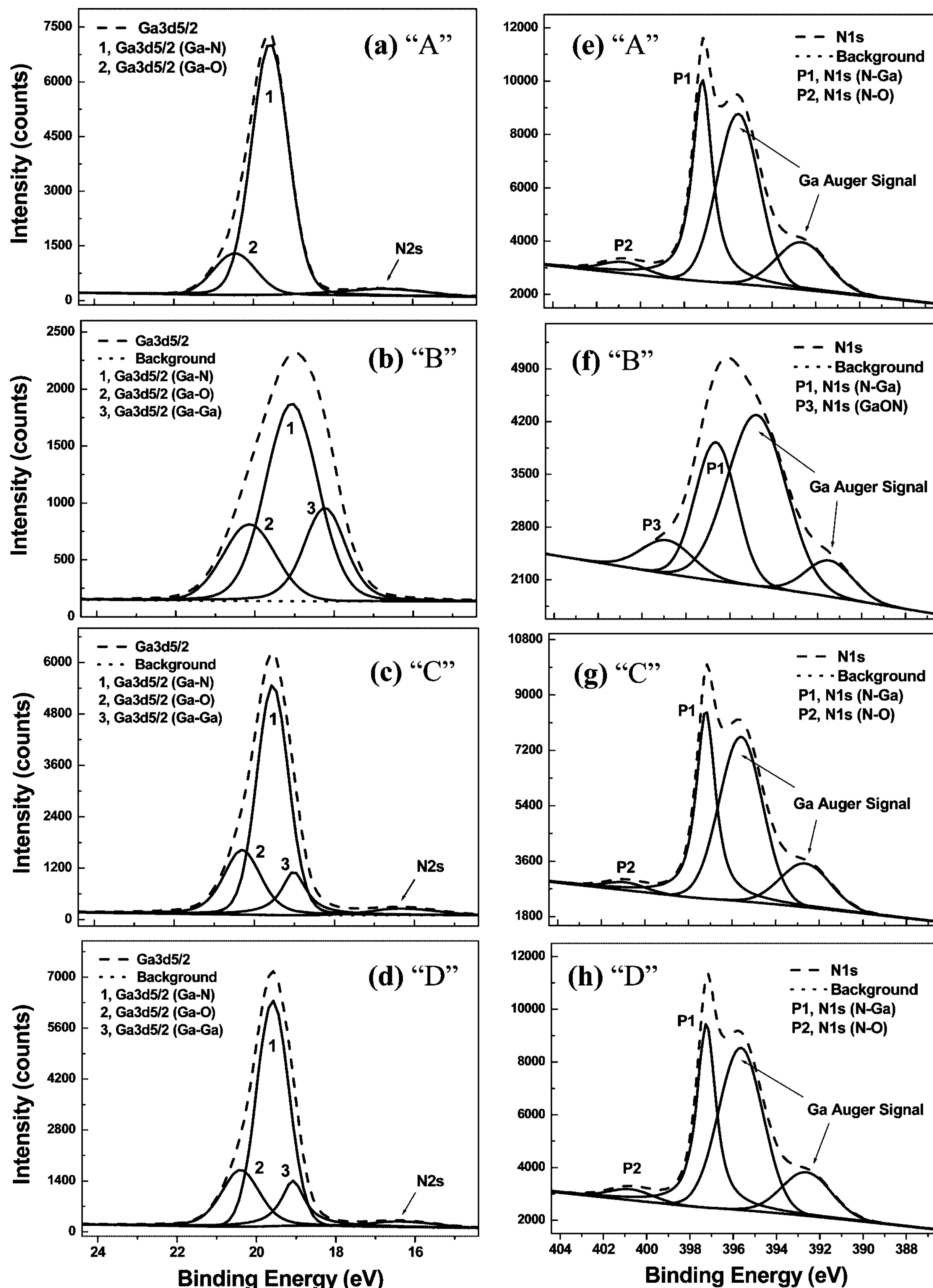

Figure 3. XPS spectra of Ga3d5/2 photoelectron peak of (a) "A", (b) "B", (c) "C", and (d) "D", and N1s photoelectron peak of (e) "A", (f) "B", (g) "C", and (h) "D". In the figure, the fitted peaks "1" (19.54 eV), "2" (20.3 eV), "3" (18.95 eV), "P1" (397.7 eV), "P2" (400.7 eV), and "P3" (399.0 eV) correspond to Ga3d5/2 (Ga−N), Ga3d5/2 (Ga−O or Ga−ON), Ga3d5/2 (Ga−Ga), N1s (N−Ga), N1s (N−O), and N1s (GaON), respectively.

intensity of P2 was not included because it was from surface contamination after exposure to air as described above. From the integrated peak intensities of different chemical components we obtained $X_{Ga/N}^{A} = 0.92$, $X_{Ga/N}^{B} = 1.15$, $X_{Ga/N}^{C} = 1.07$, and

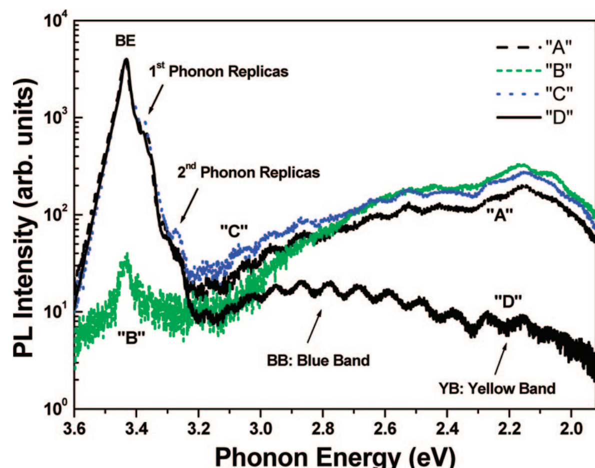

Figure 4. Room temperature (300 K) PL of GaN films at different stages: "A", "B", "C", and "D". In the figure, BE stands for band-edge emission (3.432 eV), BB blue band (centered at 2.8 eV), and YB yellow band (centered at 2.2 eV).

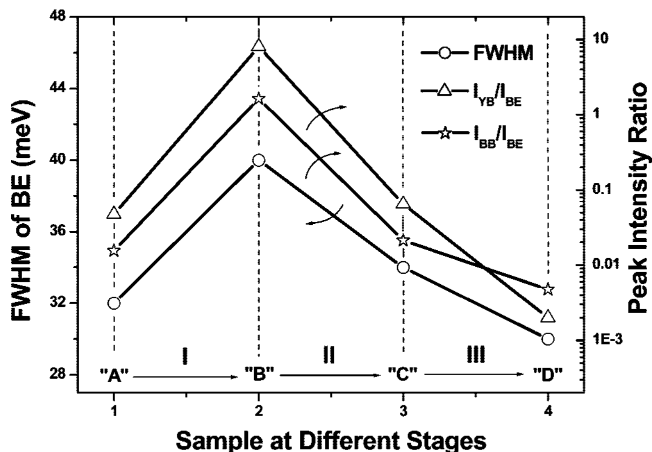

Figure 5. Fwhm of BE and peak intensity ratio of BB and YB to BE for 300 K PL of GaN samples at different stages, where BE stands for band-edge emission, BB blue band, YB yellow band, and I intensity.

$X_{Ga/N}{}^{D} = 1.04$, respectively. This indicates that the untreated GaN films were surface N-rich whereas the treated GaN films were surface Ga-rich (or close to stoichiometry).

As described in the previous section, after flowing the GaN surface with TMGa in the ambient of H_2 and NH_3 at 500 °C and 500 Torr (stage "I"), the surface became rough with islandlike surface structure (see Figure 2b). Additionally, the photoelectron peaks were broadened (Figure 3b,f for "B"). The peak broadening was mainly caused by the increased contribution from the chemical components of metallic Ga and GaON. The newly arising peak for metallic Ga (peak "3") has evidenced the formation of Ga-rich surface.

By high-temperature postannealing in H_2 and low NH_3 ambient (stage "II") the low-temperature GaN layers easily decomposed and desorbed;[33] some of the Ga atoms reincorporated to form Ga droplets, which partially reacted with NH_3 again to form nanoislands or a new "wetting layer" on the untreated GaN films. The "wetting layer" surface is smooth of layer structure with very thin droplets/nanoislands (0.3 nm) on top of it (see Figure 2c). In comparison with the XPS spectra of "B", the photoelectron peaks of "C" became sharper. In addition, "P3" disappeared, demonstrating the decomposition of the chemical component GaON and desorption of oxygen in H_2 ambient and at high temperature. By a close view of the peak shapes we found there was a small broadening for "C" (Figure 3c) compared with that of "A" (Figure 3a). The broadening of the Ga3d spectrum was due to the increase of peak intensity for the chemical component Ga. As a result based on the AFM and XPS measurements, the sample "C" surface was characterized as Ga droplets/nanoislands patterned layer-structured surface with a Ga/N ratio of 1.07. Further droplet homoepitaxy of GaN (stage "III") resulted in the coarsening of droplets/nanoislands and reduction of island density (see Figure 2d) with a surface Ga/N ratio of 1.04 (from Figure 3d,h). The nonstoichiometry of the GaN surface/interface is usually correlated with native point defects and impurities. After surface modification, the sample surface/interface becomes closer to stoichiometric (Ga/N ratio of 1.04).

c. Comparisons of the Luminescence Properties. Figure 4 shows the 300 K PL spectra for the GaN films "A", "B", "C", and "D". Three common GaN PL bands, i.e., band-edge emission (BE, 3.432 eV), blue band (BB, 2.8 eV), and yellow band (YB, 2.2 eV), are clearly observed. For samples "A", "C", and "D", additional peaks corresponding to the first and second phonon replicas of BE are also clearly visible; further, the observation of Fabry−Perot interference fringes indicates a smooth surface/interface formed, which is consistent with the previous AFM results.

The full-width-at-half-maximum (FWHM) of the BE emission for untreated GaN sample is 34 meV. After stage "I" treatment (sample "B") the 300 K PL shows a broadening of the BE with a FWHM of 40 meV and interestingly a strong reduction of the BE intensity. This implied that (a) the GaN nanoislands formed by stage "I" treatment at low temperature were not crystalline and (b) the BE from the bulk of "A" was strongly absorbed by the newly formed noncrystalline GaN nanoislands.

During the stage "II" treatment process, GaN decomposition and Ga desorption populated.[33] The GaN nanoislands decomposed, desorbed, and evaporated and some Ga reincorporated to form Ga metal droplets, Ga-rich GaN nanoislands, and thin "wetting layers" (transformed from the GaN nanoislands by annealing) on the layer-structured surface (see Figure 2c). The 300 K PL of sample "C" is similar to that of "A" with a small red shift of BE by 2 meV and a small increase of the BB/YB intensity. The red shift indicates the compressive strain relaxation by formation of Ga-rich nanoislands. The small increase of yellow/blue emission intensity was possibly from the "wetting layers" transformed from postannealing of the GaN nanoislands.

On the droplets/nanoislands patterned Ga-rich surface GaN droplet homoepitaxy was carried out at high temperature with low ammonia flow rate ("D"). Both Ga-rich surface and high temperature are favorable for the growth of high-quality GaN films (surface/interface) due to the enhanced adatom diffusion.[17,29,30] Low ammonia flow rate was employed for elimination of Ga vacancy and its complexes with O ($V_{Ga}-O_N$),[36] which has been considered as the main source of YB.[2,37] By such an in situ three-step treatment, significant reduction of YB/BB emissions has been achieved for sample "D".

In summary, we show in Figure 5 the trends for the FWHM of BE and the peak intensity ratio of YB/BB to BE. Briefly, the fwhm initially increased from 32 to 40 meV when the untreated GaN surface was flowed with TMGa at low temperature; after annealing the FWHM decreased to 34 meV due to the decomposition and desorption of GaN nanoislands formed at the first-step treatment; finally with TMGa flow to the surface at high temperature and low ammonia flow rate, the FWHM further decreased to 30 meV. In comparison with the intensity

of BE, the YB/BB intensity first increased and then decreased quickly, which is similar to the trend of FWHM of BE. After surface modification the peak intensity of BB/YB to that of BE drastically decreased from 0.0155/0.048 to 0.005/0.002 demonstrating significant improvement of the surface/interface qualities.

For further comparisons/discussions, we also prepared sample "G" with treatment processes similar to that of "D" except for step "I". Details for the XPS and PL data of "G" can be found in the Supporting Information. Briefly, the XPS data show a $X_{Ga/N}^{G}$ of 1.07, slightly larger than that of "D". By comparison of the optical properties, the FWHM of BE for sample "G" is 38 meV, also larger than that of "D" (30 meV). The 300 K PL measurements show stronger yellow (blue) luminescence for "G", i.e., about 3 (5) times of that for sample "D". This suggests that, without the first-step treatment, impacts of improvement in optical properties (i.e., reduction of BB/YB emissions and decrease of FWHM of BE) by surface modification would be weakened.

IV. Conclusion

An in situ three-step surface treatment technique was employed to modify the surface properties of GaN films. By flowing the untreated sample surface with TMGa in H_2 and low NH_3 ambient at low temperature followed by high-temperature annealing, Ga droplets and GaN nanoislands were formed on the surface. On the patterned surface droplet homoepitaxy of thin GaN layers was realized by flowing the sample surface with TMGa and low NH_3 for 400 s in H_2 ambient at 1035 °C. We find the surface treatment processes not only influenced the growth behavior and surface morphology but also modified the surface chemistry from N-rich to surface stoichiometry close to 1. Further photoluminescence studies also showed significant reduction of yellow (blue) luminescence from the treated GaN films to about 1/24 (1/3) of that from the untreated GaN films.

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Supporting Information Available: XPS and PL data of sample "G" treated without the first-step treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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