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Processing and structure of gallium nitride—gallium oxide platelet nanostructures

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Abstract

Gallium nitride–gallium oxide structures were formed by heat-treating gallium nitride (GaN) powders in several gas environments at temperatures from 400°C to 900°C. The platelet nanostructured particles were examined at several stages of oxidation by microscopic, structural, chemical and optical spectroscopic techniques. Particle morphology, nanophase characterization and photoluminescence data showed that the oxide layers passivate the GaN platelets surfaces and significantly reduce the yellow emission while enhancing near band-edge emission.
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Keywords: GaN; Ga_2O_3; Nanoparticles; Core–shell structure; Quantum confinement effect; Quantum well; Yellow emission; Surface passivation; Controlled oxidation

I. Introduction

The synthesis of nanometer size clusters and powders of electronic and optical materials is an important aspect of the applied physics of materials for new devices. Nanoparticle synthesis in the size range of 1–10 nm is an especially attractive option for achieving quantum confinement effects creating a novel "band structure engineering" approach to semiconductor materials processing. In the past few years, the field of nanostructure science and technology has become a broad interdisciplinary area of research. In the previous work of our group, we have reported the synthesis and optical properties of nanoparticles of a number of II–VI and III–V semiconductors formed in solutions, glasses, and polymer matrices. Specially interesting are studies of gallium nitride (GaN) and the related wide band gap III–V nitride semiconductors which have been particularly researched for applications such as blue/green lasers, flat panel displays and other devices. Many different routes have led to the successful synthesis of nanocrystalline group III-nitrides, especially GaN, include pyrolysis of organogallium compounds [1–3], laser ablation [4–6], and other chemical or hybrid methods. Composites of GaN nanoparticles in polymer [7] or silica gel matrices [8,9] through the use of organogallium precursors have also been reported. We have recently reported that ordered arrays of amorphous GaN can be synthesized in block copolymers with controlled architectures [10,11].

Attaining precise stoichiometry remains an important synthesis challenge in GaN and related nitride semiconductors. Typically, the N/Ga ratio of as-synthesized GaN is less than 1 (usually in the range 0.85–0.99). The nitrogen deficiency in the crystal structure generates free electrons giving rise to n-type GaN. From an optical properties perspective, the photoluminescence (PL) spectrum of undoped GaN shows a characteristic broad yellow emission, peaking near 2.2 eV, and a near-band-edge peak at about 3.35 eV. The existence of this yellow emission greatly degrades optical properties of GaN and synthesis efforts focused on suppressing yellow emission while enhancing the near band-edge emission are worthwhile to fully realize the potential of GaN as an optical material.

In the present work, we report the preparation of core–shell-like gallium oxide (Ga_2O_3) capped GaN

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nanoparticles by oxidizing the surfaces of platelet-like GaN powders at high temperatures in ammonia (NH_3) and nitrogen (N_2) gas atmospheres. The structural, chemical, and optical luminescence data on the heat-treated nanoparticles are subsequently analyzed in relation to the yellow emission in GaN which may originate from nitrogen vacancies, gallium interstitials, defects such as dislocations, impurities, or surface-dangling bonds.

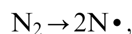
2. Experimental procedure

GaN powders obtained from a commercial source (Atomergic Chemicals Corp.) were heat treated in a conventional atmosphere-controlled tube furnace. Heat-treatment temperatures ranged from 400°C to 900°C, and time ranged from 0.5 to 192 h, with a flowing stream of NH_3, N_2 gases or their mixtures circulating at a flow rate of 100 mL/min. Following heat treatment, the platelet-like particles were characterized by a number of microscopic and optical techniques. X-ray diffraction (XRD) spectra were obtained with a Scintag XDS-2000 diffractometer. Scanning electron microscopy (SEM) images were obtained using a field emission gun (FEI XL-30S FEG) microscope. The particles were suspended in methanol and dispersed on to holey-carbon-coated 400 mesh copper grids for transmission electron microscopy (TEM) analysis and high-resolution TEM (HRTEM) images were collected on Philips CM-300 transmission electron microscopes. For the atomic force microscopy (AFM) experiments, samples were prepared by suspending GaN particles in methanol and spin coating on to cleaned silicon wafers. Finally, solid state nuclear magnetic resonance (NMR) data were collected by a Chemagnetics CMX-400 spectrometer, operating at 122.03 MHz (^{71}Ga) under magic angle spinning (MAS) conditions using a frequency of 16.2 kHz. PL spectra were obtained with a Perkin Elmer LS-50B luminescence spectrometer, operating at room temperature without using filters. The lamp source is pulsed xenon with an average energy 0.15 J/flash.

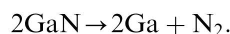
3. Results and discussion

Possible reactions [12–15] during the heat-treatment procedure we used were as follows:

$$NH_3 \rightarrow N\bullet + 3H\bullet,$$



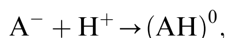
$$N_2 \rightarrow 2N\bullet,$$



$$2GaN \rightarrow 2Ga + N_2.$$

The generated N and H species (free radicals, cations and ions) are highly reactive and can further react with N deficiencies, acceptor and donor states in GaN

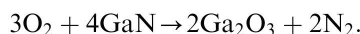
$$N\bullet + (\text{N deficiency}) \rightarrow GaN,$$



$$A^- + H^+ \rightarrow (AH)^0,$$

$$D^+ + e^- + H^0 \rightarrow (DH)^0,$$

where A^- is acceptor, $(AH)^0$ is acceptor pair, D^+ is donor, and $(DH)^0$ is donor complex. And, O_2 reacts with GaN to form β-Ga_2O_3 (monoclinic)



$$3O_2 + 4GaN \rightarrow 2Ga_2O_3 + 2N_2.$$

Previous reports [16–19] point to possible origins of yellow emission in GaN notably focused on N deficiency which can be either N vacancies or gallium (Ga)

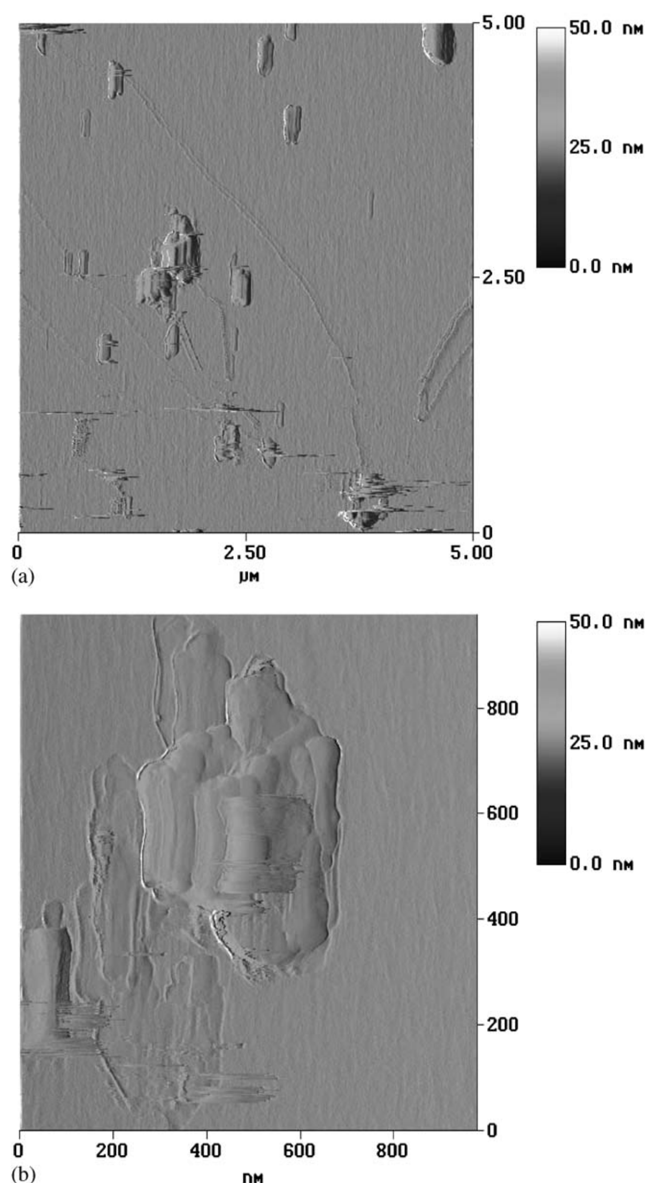


Fig. 1. Atomic force microscope (AFM) images of GaN nanoplatelets (as small as 50 nm thick in the photograph of (a) and agglomerated platelets clumped to form clusters up to 300 nm in size (b).

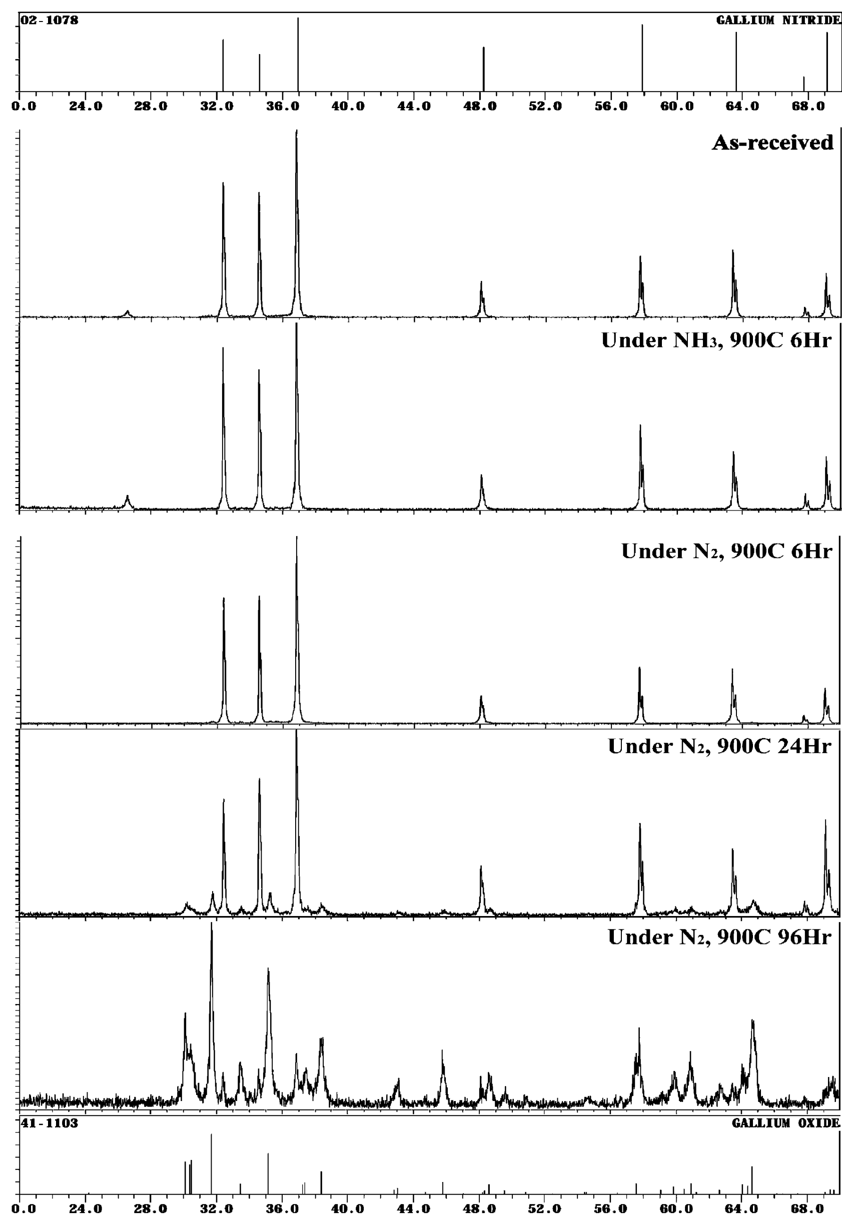


Fig. 2. X-ray diffraction data for a series of GaN samples showing the evolution of β-Ga_2O_3 with oxidation upon heat treatment under nitrogen or ammonia gas atmospheres at a number of temperatures.

interstitials. Theoretical simulations show that these defects can generate shallow donor and deep acceptor states, which might contribute to the yellow emission [20]. Other sources of yellow emission can be dislocations, impurity, surface-dangling bonds, or Ga vacancies [21] in the GaN. In our experiments, heat treating under NH_3 or N_2 mixture can cause a highly reactive N species to react with N deficiency centers and effectively remove these N vacancy and Ga interstitial states. Moreover, when heat treating under NH_3, H species can further passivate possible acceptor or donor states in GaN. Based on these concepts one should expect significant changes in optical properties by lowering the concentration of N vacancies.

AFM images (Fig. 1) show the morphology of the GaN particles as hexagonal platelets with some features as large as 300 nm. However, the thickness of these platelets is much smaller (about 50 nm). The nanoplatelets sometimes aggregate to form agglomerates. X-ray diffraction (XRD) patterns of as-received and heat-treated GaN particles are shown in Fig. 2. There are no structural changes of GaN detected after heat treatment under either NH_3 or N_2. For GaN samples heat treated under N_2, because of the oxygen leakage into the reaction chamber as well as oxygen impurity in the N_2, (β-)Ga_2O_3 peaks (e.g. at 31.719° and 35.208°) appear due to surface oxidation of GaN platelets. As the heat-treatment time increase, the Ga_2O_3 peaks get stronger,

indicating greater degree of oxidation. Note that characteristic peaks at 32.443°, 34.637°, and 36.998° in XRD spectra (heat treated under N_2 at 900°C for 96 h) clearly confirm the existence of GaN. Combined with AFM images, the XRD data suggests that a GaN–Ga_2O_3 core–shell structure is being created by the heat treatment under N_2.

^{71}Ga-NMR spectra of GaN under static and MAS conditions are shown in Fig. 3. For as-received GaN, two peaks can be identified from static and MAS spectra. The strong and sharp peak at 333 ppm is from GaN, and the side peak at about 407 ppm is probably from defect states in GaN [22]. For heat-treated (N_2, 900°C for 6 h) GaN, an extra very broad peak (from 233–(-)344 ppm) appears in both the static and MAS spectra. This peak is from Ga_2O_3 as also reported in other NMR studies of β-Ga_2O_3 [23]. The NMR results suggest that no major changes of local atomic structure were detected. For the heat-treated sample, the GaN peak (chemical shift = 333 ppm) intensity decreases due to the conversion of GaN into Ga_2O_3. These data suggest that while the GaN platelet surfaces are oxidized impurity/defects states are not significantly altered.

SEM images of GaN again show the morphology of plate-like structures and the smaller granules at the surfaces of these plates (Fig. 4a and b). Fig. 4c and d are the SEM images of GaN heat-treated under NH_3 at 900°C for 6 h. They show that NH_3 react with GaN platelets (both from the top and bottom surfaces) and the newly formed GaN structures are aligned in the (0001) direction. Fig. 4e and f are SEM images of GaN heat treated under N_2 at 900°C for 6 h. They show that heat treating under N_2 causes scale-like oxide structures to form on GaN surfaces. At longer heat-treatment time, many of the small scales in Fig. 4e and f fuse into much larger oxide islands (Fig. 4g and h). Fig. 4g also suggests that the scale-like structures first form a larger closely packed cover on each face of GaN plate-like particle, then crack into islands during the period of cooling down due to thermal expansion difference between Ga_2O_3 outer shells and GaN inner cores. This leads to the formation of GaN–Ga_2O_3 core–shell structures. One possible effect of this surface oxidation could be that the Ga_2O_3 outer shell passivates the surface-dangling bonds of the GaN. Preliminary data of the structure of two selected samples of these core–shell materials were also obtained by high-resolution TEM imaging [24]. For example, a sample of GaN heat treated under N_2 at 900°C for 6 h showed lattice fringes whose spacing could be determined from enlarged images (these data confirmed the presence of both GaN and Ga_2O_3 regions in this sample); the sample heated for 96 h revealed no GaN lattice fringes suggesting the complete oxidation of the surfaces and edges of these platelets. These preliminary data point to the need for a more detailed investigation by high-resolution TEM techniques.

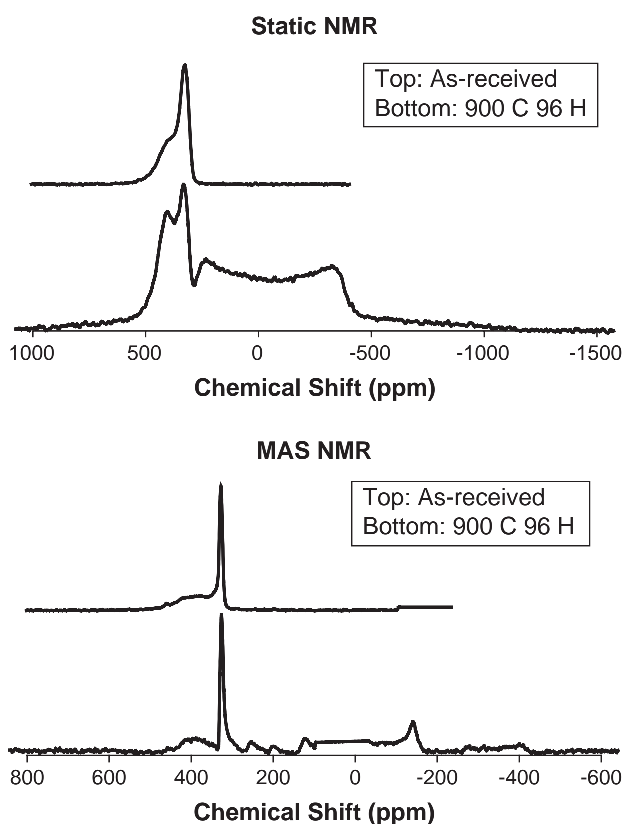


Fig. 3. Nuclear magnetic resonance (NMR) spectra of GaN under static and MAS conditions. The extra broad peak in the lower part of each spectrum is from Ga_2O_3 formed on GaN platelet surfaces upon heat treatment.

Chemical analysis results of heat-treatment effects on GaN are shown in Fig. 5. Clearly the heat treatment in NH_3, N_2 or their mixtures can efficiently increase the N content of GaN platelets. Heat-treating GaN under NH_3:N_2 = 3:1 increases N content up to ~16.65% in weight, which is very close to the stoichiometric value, 16.73% in weight. This small deviation from stoichiometry could be due to either N vacancies or merely slight errors in chemical analysis. These results also show that the NH_3–N_2 mixtures must have higher reactivity than pure NH_3 or N_2 or lead to an increase in the N_2 partial pressure that can effectively suppress the GaN dissociation reaction. It can also be inferred that the heat treatment under N_2 alone causes surface oxidation and creation of GaN/Ga_2O_3 structures.

Selected PL spectra of untreated and heat-treated samples are shown in Fig. 6a–d. Since the central focus of the present work is structural changes of GaN during processing, we only report relative changes of near band-edge and yellow-emission peaks at room temperature. We used excitation wavelengths from 280 to 340 nm without an optical filter to obtain the PL data. The PL spectra of the as-received GaN and the GaN heat treated under NH_3 at 900°C for 6 h (Fig. 6a and b)

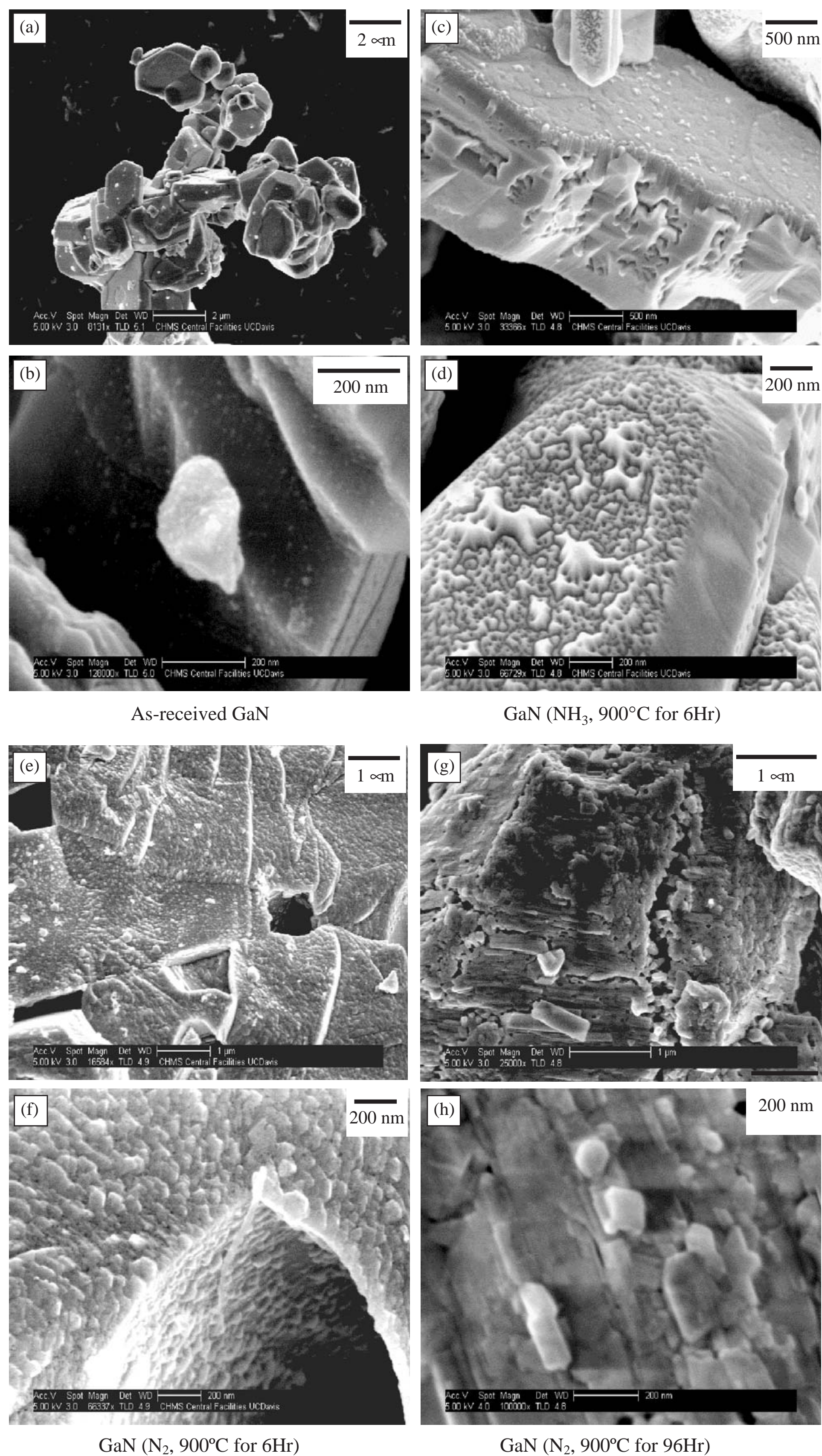


Fig. 4. Scanning electron microscope (SEM) images of a number of GaN samples in various stages of morphological evolution as heat treatment proceeds. (a) and (b) as-received GaN; (c) and (d) GaN heat treated under NH_3 at 900°C for 6 h; (e) and (f) GaN heat treated under N_2 at 900°C for 6 h; (g) and (h) GaN heat treated under N_2 at 900°C for 96 h. Oxidation is first detected as shown in (c) and (d) and progresses to scale formation and some fusing of particles (e)–(h).

are very similar. This indicates that N enrichment (as indicated by chemical analysis) towards a more stochiometric GaN material does not appear to lead to improved optical properties. The PL spectra of GaN heat treated under N_2 at 900°C for 6 h (not shown) are almost identical to the spectra of under NH_3 condition. The PL spectra of GaN heat treated under N_2 at 900°C for 24 h (Fig. 6c), however, show a slight increase in the intensity ratio of near band-edge emission/yellow emission. By contrast, continued heat treatment for longer time, 96 h, give PL spectra (Fig. 6d) that are quite dramatically different: the yellow emissions (470–610 nm) are greatly suppressed while the near band-edge emissions (~370 nm) get enhanced. This, again, suggests that N deficiencies are not the origin of yellow emission in GaN.

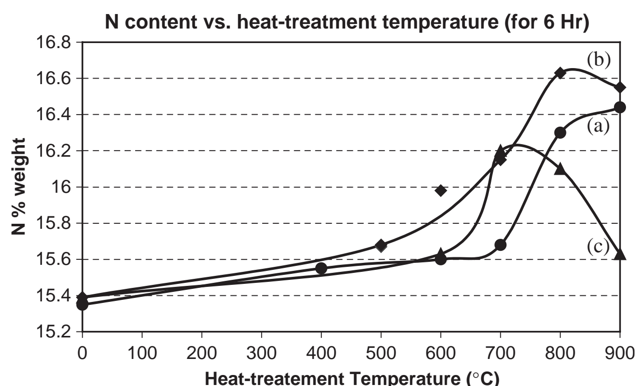


Fig. 5. Effect of heat treatment in various atmospheres on the bulk (chemically analyzed) nitrogen content of the GaN particles (all heat treated for 6 h). (a) under NH_3; (b) under NH_3:N_2 = 3:1; (c) under N_2.

Coupling these PL data with the structural and chemical results discussed earlier, it is reasonable to conclude that the surface oxidation of GaN platelets to form Ga_2O_3 is related to the reduction of yellow emission. It is likely that surface-dangling bonds at GaN surfaces are the origin of the yellow emission. The Ga_2O_3 layer must passivate the GaN surface as it forms the core–shell structure under certain heat-treatment conditions. In the process, the concentration of GaN surface-dangling bonds decreases, and radiative recombination of electrons and holes overwhelms non-radiative recombination, which in turn leads to the suppression of yellow emission and enhancement of near-band-edge emission. Furthermore, the observed shifts in PL at the near band-edge emission could be due to quantum confinement effects. As Ga_2O_3 layers form from the surface towards the center of GaN, the size of the GaN platelets gets smaller and smaller eventually reaching dimensions comparable to or less than the exciton Bohr dimensions. While this hypothesis has not been fully demonstrated in the present work it is tempting to suggest that similar oxidized surface structures may prove beneficial in processing other III–V and II–VI materials in nanowire, nanorod and

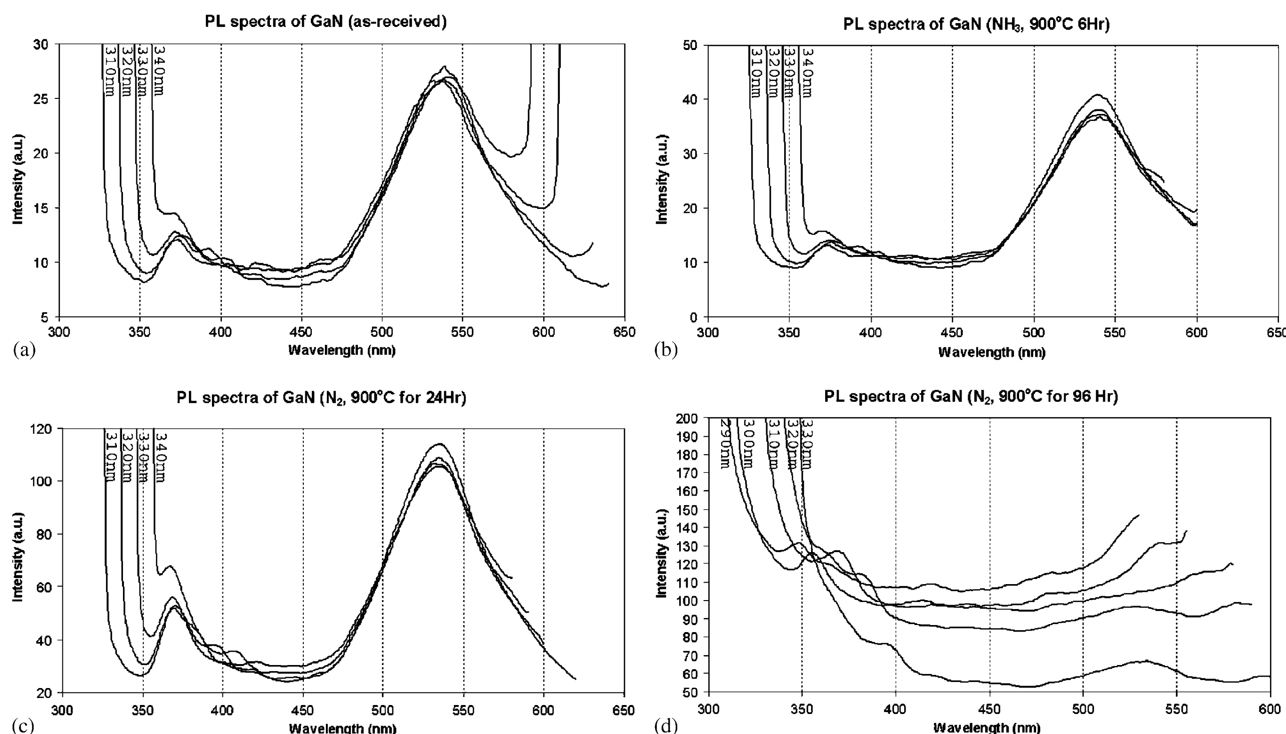


Fig. 6. PL spectra of a series of GaN samples with successive heat treatments. The PL spectra in (a)–(c) show little changes but dramatic changes can be seen in the spectra shown in (d), which shows enhanced emission at the 370 nm band-edge and reduced yellow emission.

nanodot morphologies with attendant enhancement of optical or electrical properties.

4. Summary

GaN particles in platelet morphologies were oxidized to form GaN–Ga_2O_3 core–shell-type structures upon long-heat treatment in nitrogen. The Ga_2O_3 layers passivate the GaN surfaces of the platelets effectively reducing the number of surface-dangling bonds and suppressing the yellow emission while enhancing near band-edge emission. The PL and chemical analysis data suggest that nitrogen deficiency (vacancies) is not the sole origin of the yellow emission in GaN.

Acknowledgments

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