

# Communications

## Influence of Precursor Route on the Photoluminescence of Bulk Nanocrystalline Gallium Nitride

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Received July 22, 1997

Revised Manuscript Received September 30, 1997

Interest in new routes for the preparation of the wide bandgap semiconductor gallium nitride, GaN, continues to grow at a fast pace, driven primarily by the possibility of blue-emitting lasers, light-emitting diodes (LED's), and robust photodetectors based on this semiconductor.<sup>1</sup> A number of new precursor routes culminating in bulk nanocrystalline gallium nitride have recently been reported, with specific variations in the pyrolysis conditions enabling some control over the particle nanosize and a degree of crystalline phase inhomogeneity of the materials.<sup>2</sup> One viable precursor is the new polymeric gallium imide  $\{\text{Ga}(\text{NH})_{3/2}\}_n$ , which can be converted to nanocrystalline, cubic/hexagonal GaN via deamination.<sup>2b</sup> Another method involves a new route to cyclotrigallazane,  $[\text{H}_2\text{GaNH}_2]_3$ , from the combination of  $\text{LiGaH}_4$  and  $\text{NH}_4\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in  $\text{Et}_2\text{O}$ .<sup>2c</sup> Under employed conditions, this latter precursor is known to slowly convert to a polymeric solid by  $\text{H}_2$  and  $\text{NH}_3$  elimination–condensation pathways.<sup>2c</sup> Both the cyclotrigallazane and the polymeric solid have been shown to be viable precursors for pyrolysis to nanocrystalline, phase-inhomogeneous GaN via dihydrogen elimination.<sup>3</sup> For both the gallium imide and gallazane precursors, it is critical to assess the impact of specific preparative conditions on the luminescence of the resultant nanophase GaN materials which are formed. Such measurements are useful in this context as a means of assessing the presence of defect or nonradiative sites in the solid(s). In regard to the luminescent spectral behavior of GaN,

generally intrinsic bandgap photoluminescence (emitting in the blue region with a maximum near 410 nm) and/or broad defect photoluminescence (known to emit in the yellow region<sup>4</sup>) can be observed in principle. It should be stressed, however, that nonradiative states which lower the observed quantum yield of band edge and/or defect photoluminescence can also play a role.

The preparation of the polymeric gallium imide  $\{\text{Ga}(\text{NH})_{3/2}\}_n$  was accomplished according to the published method.<sup>2b</sup> Cyclotrigallazane and the related polymeric solid were synthesized from the new reaction system  $\text{LiGaH}_4/\text{NH}_4\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in  $\text{Et}_2\text{O}$ , as described elsewhere.<sup>2c</sup> These precursors were pyrolyzed to nanophase GaN at specific elevated temperatures either under an ammonia flow and/or under vacuum (as described below; see also ref 3). In addition, a decomposition of the gallium imide was carried out in boiling  $\text{N,N,N',N'}$ -tetramethyl-1,6-hexanediamine (bp 210 °C). In all of the above reactions, analyses of the solid products by X-ray powder diffraction (XRD) and/or transmission electron microscopy (TEM) confirmed the formation of phase-inhomogeneous, nanocrystalline GaN best described as a mixture of cubic and hexagonal close-packed layers of GaN.<sup>2d,e,3</sup>

Room-temperature photoluminescence (PL) data were recorded using a SPEX Fluorolog-2 instrument equipped with a double emission monochromator and a R928 photomultiplier tube. Excitation was provided by a 450 W Xe lamp whose output was focused into a 0.22 m monochromator to provide an excitation wavelength of 325 nm. PL spectra for some samples were also recorded by excitation with the 325 nm line of a Linconix HeCd laser with an average power of 7 mW.

Here we report the luminescent properties of GaN materials derived from gallium imide and obtained as follows: (a) reflux in the  $\text{N,N,N',N'}$ -tetramethyl-1,6-hexanediamine at 210 °C for 48 h (sample a); (b) 300 °C,  $\text{NH}_3$ , 4 h (sample b); (c) 500 °C,  $\text{NH}_3$ , 4 h (sample c); (d) 600 °C,  $\text{NH}_3$ , 4 h (sample d); and (e) 600 °C, vacuum, 3 h (sample e). Representative room-temperature PL spectra for these GaN samples are illustrated in Figure 1. Pyrolysis of the gallium imide precursor at or above a temperature of 500 °C either in vacuo or in an  $\text{NH}_3$  atmosphere will typically produce GaN crystallites  $\leq 13$  nm in diameter<sup>2b,3</sup> which exhibit defect emission with a relatively low quantum efficiency. This is exemplified by the PL spectrum of GaN prepared by the pyrolysis of gallium imide at 600 °C under vacuum (sample e). Such weak PL is attributed to the presence of nonradiative defects of either interfacial or interior character.

Much stronger PL (albeit defect emission) can be observed, however, when the pyrolysis temperature is lowered or the reaction medium is changed. For example, when the gallium imide precursor is pyrolyzed

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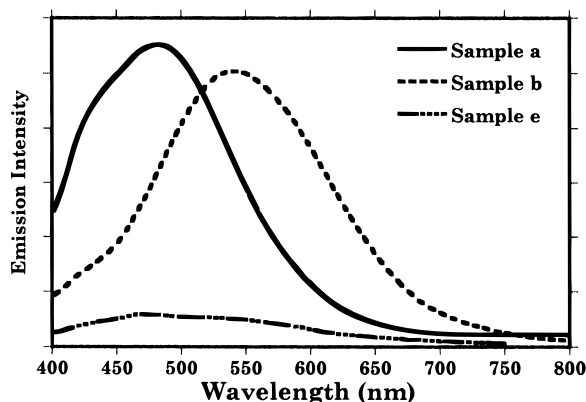
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**Figure 1.** Room-temperature PL spectra for GaN samples prepared by pyrolysis of gallium imide: spectrum a (solid line), reflux in N,N,N',N'-tetramethyl-1,6-hexanediamine, bp 210 °C, 48 h; spectrum b (dashed line), 300 °C, NH<sub>3</sub>, 4 h; spectrum e (dot-dashed line), 600 °C, vacuum, 3 h.

in an ammonia atmosphere at a lower temperature of 300 °C, a more intense defect PL spectrum with a broad peak maximum near 560 nm is observed (sample b). Measurements of the temperature dependence of the intensity of this emission from 10 to 300 K (Supporting Information) reveal an exponential behavior characteristic of multiphonon-induced radiationless processes<sup>5</sup> and similar to that previously observed for donor/acceptor emission in nanophase CdS.<sup>6</sup> It is found that a vacuum anneal of this type of GaN at 500 °C overnight results in diminution of the intensity of this band, also consistent with its characterization as defect luminescence. While the origin of this type of yellow-green PL in GaN has been the subject of intense debate,<sup>4</sup> some consensus is now emerging that the likely origin of the emission is a transition involving a shallow donor and a deep acceptor level.<sup>7</sup> The precise structural identity of the defect site in these particular nanoparticles remains uncertain; elemental analyses are consistent with the presence of some trace carbon in these samples, and FT IR measurements suggest the presence of N–H species as well. Carbon impurities could influence the formation of a C on N site defect (C<sub>N</sub>) from residual C and H supplied from [Ga(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, the starting material for the Ga imide precursor.<sup>2b,8</sup> It is also possible that structural defects (Ga vacancy, N<sub>Ga</sub> antisite) could arise in the structure of the GaN lattice formed during transformation of the precursor.

If the pyrolysis of the gallium imide is carried out in the refluxing N,N,N',N'-tetramethyl-1,6-hexanediamine (bp 210 °C), the resultant GaN emits strongly in the blue region of the spectrum (430–480 nm). This bright blue luminescence can easily be observed with the unaided eye under UV excitation (Figure 2). A close examination of the PL spectrum of GaN sample a (Figure 1) reveals the presence of a shoulder at 410 nm as well as the observed peak maximum near 480 nm. It should be noted that there can be some variance in



**Figure 2.** Blue light emission emanating from bulk nanocrystalline GaN powder (sample a) upon 325 nm excitation.

the ratio of the two features, depending on the sample. Control experiments reveal that some of the intensity of the 480 nm component originates from the pyrolyzed amine coating present on the semiconductor surface (sample a). It was thus necessary to develop a protocol to eliminate the contribution from the amine coating as well as remove surface defects. Previous accounts regarding bulk epitaxially grown GaN have demonstrated that HF and HNO<sub>3</sub> have some utility as etchants for removing oxide and hydrocarbon impurities from GaN;<sup>9</sup> Nozik and co-workers have shown recently that a brief HF etch can passivate surface defects in InP nanoparticles as well.<sup>10</sup> In another sample of GaN prepared by this same route whereby the two spectral features are of the same intensity, it is found that a brief etch (20 s) of this particular type of GaN using 48% HF narrows the observed PL line width considerably and removes the longer wavelength contribution to the observed emission, presumably from the amine coating (Figure 3a).

With regard to GaN derived from the gallazane precursors, our efforts to date have focused on samples prepared from pyrolysis of the pure cyclotrigallazane and the related polymeric solid (derived from the LiGaH<sub>4</sub>/NH<sub>4</sub>Br system) at 600 °C in an NH<sub>3</sub> atmosphere. For example, it is interesting to note that only blue emission is observed in the 13 nm GaN crystallites derived from the polymeric precursor (Figure 3b), with a PL maximum near 420 nm. There is some variation in the relative intensity of this peak from sample to sample (as might be expected), since varying amounts of excess Ga are likely to be present which act as scattering centers for the exciting light and thereby lower the observed emission intensity.<sup>11</sup> We have also evaluated the efficacy of the acids HF and HNO<sub>3</sub> on the photoluminescence of nanophase GaN prepared by this gallazane route. Samples were exposed to solutions of 35% HNO<sub>3</sub> or 48% HF for varying time intervals; in terms of improved PL properties, it is found that only HF acts to improve quantum efficiency. A very brief etch (20 s) using 48% HF followed by a water and an ethanol wash yields an improvement in the intensity of blue PL spectrum by a factor of 4 (Figure 3b).

At present, details of the mechanism of improved

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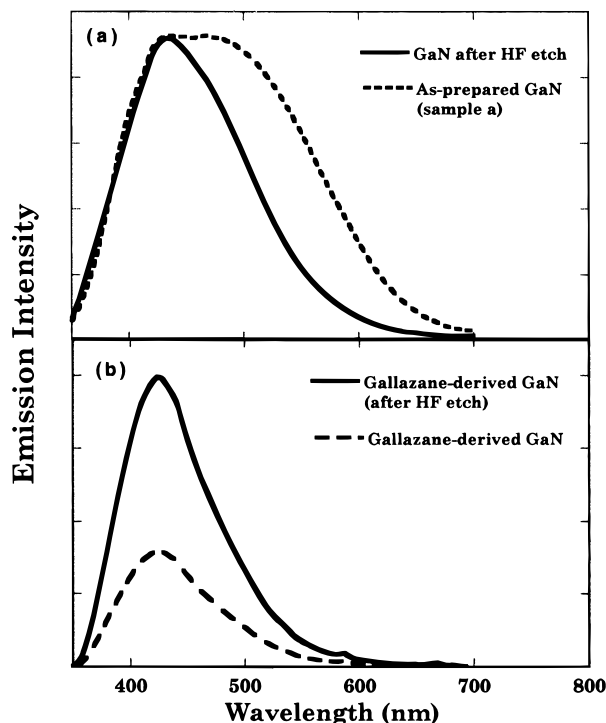
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(8) Elemental analyses for a range of related GaN samples gave Ga/N ratios between 1.02/1.00 and 1.05/1.00, carbon contents generally well below 1%, and hydrogen contents on the order of a few tenths of a percent.

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(11) The observed thermochemical instability of these precursors and available elemental analyses support gallium enrichment in the pyrolyzed GaN materials (C, H, and Li contents less than 0.1%; Ga/N ratios between 1.05/1.00 and 1.29/1.00).



**Figure 3.** (a) The effect of HF etching upon the PL spectrum of GaN prepared by pyrolysis of gallium imide by heating to reflux in  $N,N,N',N'$ -tetramethyl-1,6-hexanediamine (bp  $210\text{ }^{\circ}\text{C}$ ) for 48 h (sample **a**); (b) the effect of brief HF etching on the room-temperature PL spectrum of a GaN sample prepared by pyrolysis of the gallazane-derived polymeric solid.

luminescence for the nanophase GaN derived from either type of precursor are not clear. However, it

should be noted that if appreciable yellow defect PL is present in the original GaN nanophase product, then no conversion of defect to band-edge PL is observed upon acidic etching. It is thus likely that the removal of oxide and/or hydrocarbon-related nonradiative centers by the acid at the nanoparticle surface plays a key role in these observations. Interior defects are presumably unaffected by this process. Another important issue, the role of acid etching and other treatments on average GaN particle size (as evaluated by TEM) remains to be elucidated.

In summary, the impact of preparative method on the photoluminescence of bulk nanophase GaN materials has been evaluated. In general, the observed emission spectra are strongly dependent on the choice of precursor and the pyrolysis temperature used in its conversion to GaN. Regardless of precursor, it appears that a brief HF etch of the nanophase GaN is a suitable chemical method in enhancing the blue band-edge PL of selected samples, presumably by eliminating surface defects.

**Acknowledgment.** Financial support by the Office of Naval Research (R.L.W), the Robert A. Welch Foundation (J.L.C), and the Texas Christian University Research Fund (J.L.C) is gratefully acknowledged.

**Supporting Information Available:** Plot of the temperature dependence (10 K to 300 K) of the integrated PL intensity for GaN prepared from the gallium imide precursor pyrolyzed in an ammonia atmosphere at  $300\text{ }^{\circ}\text{C}$  (1 page). Ordering information is given on any current masthead page.

CM9705193