Gallium Nitride Powders from Ammonolysis: Influence of Reaction Parameters on Structure and Properties

Birgit Schwenzer,*,† Jerry Hu,‡ Ram Seshadri,§ Stacia Keller,†
Steven P. DenBaars,§ and Umesh K. Mishra†

Electrical & Computer Engineering Department, Materials Research Laboratory, and Materials Department, University of California, Santa Barbara, California 93106

Received June 7, 2004. Revised Manuscript Received August 11, 2004

Gallium nitride (GaN) has been prepared by the reaction of ammonia with three different gallium precursors: Gallium oxide, a mixture of gallium oxide and elemental gallium, and elemental gallium. X-ray diffraction indicates that all three starting materials yield highly crystalline wurtzite GaN particles. Solid-state ^{1}H NMR has been employed to ascertain the presence of hydrogen in the samples. The technique allows a clear distinction between structural protons and protons bound to the surface of the crystals. In addition, solid-state ^{71}Ga NMR and energy-dispersive X-ray analysis display significant differences in the material. Depending on the starting material, the GaN product consists of up to three different phases. The optical properties of the product GaN powders could be correlated to the NMR data. By converting nonluminescing GaN prepared from gallium oxide into GaN, with a bright emission at room temperature around 370 nm when excited by a 325 nm He−Cd laser, further insight was gained on the correlation of structural and optical properties of GaN.

Introduction

The electronic and optical properties of group III nitride materials are of great interest for light-emitting diodes (LEDs), lasers, and other optoelectronic devices, because of their band structures and the large range of band gap (0.7−6.2 eV) that can be covered by these nitrides and their alloys. GaN-based materials (with a band gap of 3.4 eV) especially have received a great deal of attention for their blue and ultraviolet light emission[1] and because of application in high-temperature, high-power devices.[2] In recent years studies on GaN powders, nanoparticles, and nanowires have received increasing attention.[3]

While solid or liquid precursors for both elements of the II−VI semiconducting nanoparticles[4] are readily available, ammonia is still the nitrogen source of choice for the preparation of group III nitrides, with some exceptions.[5] The most common method for the preparation of GaN nanostructures is by ammonolysis of gallium-containing powders (usually a mixture of gallium oxide and elemental gallium) at elevated temperatures.[6] None of the studies have focused on the structural and optical properties of GaN prepared by ammonolysis from different starting materials. Only relatively few wet chemical approaches to prepare GaN have been reported.[7] Overall, the properties of GaN formed from different reactions are still not sufficiently researched, and questions remain. For example, whereas the effect of doping and impurities in epitaxially grown GaN layers has been intensively studied,[8] to our knowledge little has been reported regarding the influence of crystal structure and impurities in GaN powders.

For this study, we looked at some structural and optical properties of GaN particles prepared by ammonolysis from different starting materials and under varying reaction conditions. The structural characteristics of the GaN particles prepared in this study were evaluated by X-ray diffraction (XRD) and scanning

---

* Corresponding author. E-mail: birgit@ece.ucsb.edu.
† Electrical and Computer Engineering Department.
‡ Materials Research Laboratory.
§ Materials Department.

[1] Nakamura, S.; Senoh, M.; Iwasa, N.; Nagahama, S. *Jpn. J. Appl. Phys.* **1995**, L797. Fasol, G. *Science* **1996**, *272*, 1751.

[2] Pearton, S. J.; Ren, F. *Adv. Mater.* **2000**, *12*, 1571.

[3] Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, *277*, 1287. Cheng, G. S.; Zhang, L. D.; Zhu, X. G.; Chen, S. H.; Li, Y.; Zhu, Y.; Fei, G. T. *NanoStruct. Mater.* **1999**, *11*, 421. Duan, X.; Lieber C. M. *J. Am. Chem. Soc.* **2000**, *122*, 188. Kisailus, D.; Choi, J. H.; Lange, F. F. *J. Cryst. Growth* **2003**, *249*, 106.

[4] Alivisatos, A. P.; Harris, A. L.; Levinos, N. J.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1988**, *89*, 4001. Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327. Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403. Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706. Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343. Cherniavskaya, O.; Chen, L.; Islam, M. A.; Brus, L. *NanoLett.* **2003**, *3*, 497. Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. *Nat. Mater.* **2003**, 2, 382.

[5] Wallace, C. H.; Reynolds, T. K.; Kaner, R. B. Chem. Mater. **1999**, *11*, 2299. Manz, A.; Birkner, A.; Kolbe, M.; Fischer, R. A. *Adv. Mater.* **2000**, *12*, 569. Grocholl, L.; Wang, J.; Gillan, E. G. *Chem. Mater.* **2001**, *13*, 4290.

[6] Bae, S. Y.; Seo, H. W.; Park, J.; Yang, H.; Song, S. A. *Chem. Phys. Lett.* **2002**, *365*, 525. Cheng, G.; Kolmakov, A.; Zhang, Y.; Moskovits, M.; Munden, R.; Reed, M. A.; Wang, G.; Moses, D.; Zhang, J. *Appl. Phys. Lett.* **2003**, *83*, 1578.

[7] Coffer, J. L.; Johnson, M. A.; Zhang, L. *Chem. Mater.* **1997**, *9*, 2671. Yang, Y.; Leppert, V. J.; Risbud, S. H.; Twamley, B.; Power, P. P.; Lee, H. W. H. *Appl. Phys. Lett.* **1999**, *74*, 2262. Manz, A.; Birkner, A.; Kolbe, M.; Fischer, R. A. *Adv. Mater.* **2000**, *12*, 569. Grocholl, L.; Wang, J.; Gillan, E. G. *Chem. Mater.* **2001**, *13*, 4290. Wang, J.; Grocholl, L.; Gillan, E. G. *NanoLett.* **2002**, *2*, 899. Pulchinger, M.; Kisailus, D. J.; Lange, F. F.; Wagner, T. *J. Mater. Res.* **2002**, *17*, 353.

[8] Pankove, J. I.; Moustakas T. D. *Gallium Nitride, Semiconductors and Semimetals*; Academic Press: San Diego, CA 1998; Vol. 50.

10.1021/cm049094s CCC: $27.50

electron microscopy (SEM). More unusual for the study of bulk semiconducting materials is the use of solid-state ^{1}H and ^{71}Ga NMR spectroscopy. Defects and impurities (e.g. hydrogen) in materials are easily detectable—down to the nearest neighbor atomic level—by NMR. NMR results therefore greatly complement XRD data, which only show impurities, if they have an effect on the crystal structure. In combination with the observed optical properties of the GaN particles, we were able to relate the structural and optical properties of the synthesized GaN powders and also successfully converted nonluminescing GaN into luminescing GaN.

We and others have recently reported the preparation of InN nanostructures[9] by ammonolysis using only indium oxide as the starting material. In this contribution, we similarly report GaN powders prepared by the ammonolysis of Ga_2O_3 (method a). We have also used a mixture of Ga_2O_3 and elemental Ga (method b) as the Ga source for ammonolysis.[6] This method has been most commonly used for the preparation of GaN nanostructures, since the mixture of starting material yields the more volatile suboxide GaO, which then reacts with ammonia in the vapor phase to yield GaN. The third precursor we used in this study to prepare GaN particles by ammonolysis was elemental Ga (method c). This approach has been reported by Roh et al.[10]

$$Ga_2O_3 + 2NH_3 \rightarrow 2GaN + 3H_2O \qquad \text{(method a)}$$

$$Ga_2O_3/Ga + NH_3 \rightarrow GaN + \ldots \qquad \text{(method b)}$$

$$Ga + NH_3 \rightarrow GaN + {}^3/_2H_2 \qquad \text{(method c)}$$

Experimental Section

Ammonia (anhydrous grade 4.0, Airgas), Ga_2O_3 (99.999% pure, Alfa Aesar), and Ga pellets (99.999 99% pure, Alfa Aesar) are commercial products and were used without further purification. Alumina boats (Alfa Aesar) used for the ammonolysis were heat-treated under ammonia at 1100 °C for 3 h prior to use and stored under nitrogen until needed.

Approximately 0.1 g of Ga_2O_3 powder was taken in an alumina crucible. The crucible was then loaded into a quartz Schlenk tube (2.5 cm diameter) and placed in a tube furnace. The crucible containing the Ga_2O_3 was placed directly on top of the thermocouple of the furnace to minimize differences between thermocouple and actual sample temperature. After loading the Ga_2O_3, the Schlenk tube was purged with nitrogen for 30 min prior to heating. Then the nitrogen flow was turned off and the ammonia flow was adjusted to 30 sccm for all experiments unless mentioned otherwise. Ammonolysis reactions were carried out at 1000 and 1100 °C. The Ga_2O_3 was then heated under a constant ammonia flow to the desired temperature at a rate of 10 K/min and held at the reaction temperature for 2 h. At the end of the heating period, the quartz tube was cooled to room temperature within 60 min. The ammonia flow was continued until the quartz tube had reached 300 °C. For the reactions using a Ga_2O_3/Ga mixture (about 0.15 g Ga_2O_3 and about 0.4 g Ga) or only elemental Ga (about 0.4 g), the handling and heating sequence were the same. The reaction temperature was 1100 °C, because below this temperature no reaction between the metallic Ga pellet and the ammonia was observed. At temperatures below 1100 °C, the unreacted Ga was retrieved at the end of a heating cycle, only slightly deformed during the melting process.

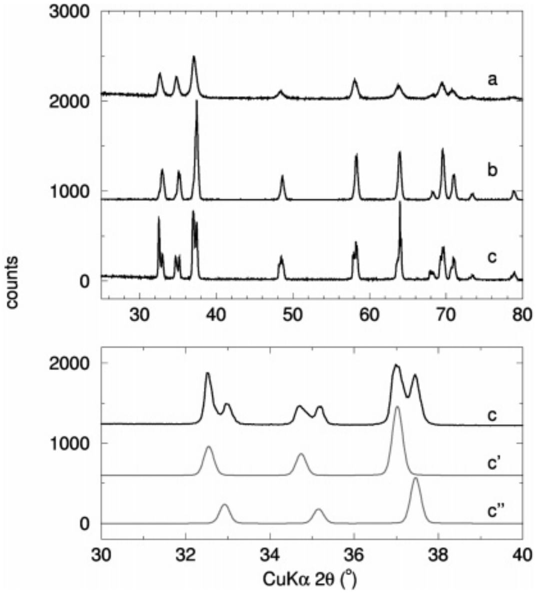

Figure 1. (Upper panel) X-ray diffraction pattern of GaN powders prepared by ammonolysis of different starting materials: from Ga_2O_3 (a), from Ga_2O_3/Ga (b), from elemental Ga (c). (Lower panel) Enlargement of pattern c (GaN prepared from elemental Ga by ammonolysis) and component of the Rietveld profile refinements (c′ and c″) for the two distinct wurtzite phases.

The GaN products were characterized and studied using powder X-ray diffraction (XRD, Philips XPERT Powder Diffractometer, Cu Kα radiation, Bragg−Brentano geometry), ^{1}H and ^{71}Ga NMR spectroscopy (Bruker DMX 500), and scanning electron microscopy (SEM, JEOL 6340F). For photoluminescence studies, a He−Cd laser (325 nm, 300 K) was used as the excitation source. Energy-dispersive X-ray spectroscopy (EDS) analysis and optical microscopy was performed by Rocky Mountain Laboratories.

Results

The GaN particles obtained from ammonolysis of the different starting materials varied significantly in their appearance. GaN prepared by method a from Ga_2O_3 at 1000 °C was homogeneous and beige-yellow in color. When the same reaction was carried out at 1100 °C, the resulting powder was slightly darker in color, beige-gray, but still appeared homogeneous. The material prepared according to method b resulted in darker, for the most part metallic gray material with some darker gray regions. Preparation of GaN particles using method c yielded similarly metallic gray material, containing some dark gray areas as well as some beige-yellow sections. The beige-yellow material in this sample resembled the GaN prepared from Ga_2O_3 at 1000 °C in color.

Figure 1 displays the powder XRD patterns of GaN crystals prepared by different ammonolysis reactions. All three methods (a−c) yield crystalline wurtzite GaN.

All XRD patterns shown in Figure 1 were recorded from the as-synthesized powders. No separation of the visibly different phases of the material prepared by method b or c was possible; therefore, the phases could not be examined separately by XRD. Considering that the GaN yielded by ammonolysis of Ga_2O_3/Ga (method b) did not appear homogeneous in color, it was unex-

---

(9) Murali, A. K.; Barve, A. D.; Risbud, S. H. *Mater. Sci., & Eng. B* **2002**, *96*, 111. Schwenzer, B.; Loeffler, L.; Seshadri, R.; Keller, S.; Lange, F. F.; DenBaars, S. P.; Mishra, U. K. *J. Mater. Chem.* **2004**, *14*, 637.

(10) Roh, C. H.; Park, Y. J.; Kim, E. K.; Shim, K. B. *J. Cryst. Growth* **2002**, 237−239, 926.

pected to detect only one set of signals for hexagonal GaN in the XRD spectrum (Figure 1b).

For the particles prepared from elemental Ga (method c), a second XRD pattern, indicating an additional hexagonal phase of GaN, was detected (Figure 1c). Although optical microscopy revealed three phases of different color for this sample, only two were observed by XRD. An enlargement of the XRD pattern of this material is shown for the region between 30° and 40° in the bottom panel of Figure 1. Rietveld refinements[11] on the XRD data of the material prepared from all three different starting materials were done, and the simulated Rietveld profile of the two phases detected in the XRD data of GaN prepared from metallic Ga is shown below the extended region of c (gray lines, c′ and c″). For the XRD pattern of GaN prepared according to method a, lattice parameters of $a = 3.185(1)$ Å and $c = 5.179(1)$ Å were determined. These are in good agreement with reported data for bulk GaN. The XRD pattern of GaN prepared according to method b gave similar lattice parameters of $a = 3.1978(2)$ Å and $c = 5.199(1)$ Å. The lattice parameters for the two phases seen in the XRD spectrum of GaN prepared from elemental Ga (method c), however, varied significantly from the values expected for crystalline GaN. In both cases, the values were smaller with $a = 3.176(1)$ Å and $c = 5.164(1)$ Å and $a = 3.141(1)$ Å and $c = 5.105(1)$ Å, respectively. Neither of the lattice parameters of the two phases could be attributed to an impurity of metallic Ga. They both indicate the presence of hexagonal GaN with unexpectedly small lattice parameters.

Scherrer broadening[12] suggests that the crystalline correlation length of GaN prepared from Ga_2O_3 (method a) was the smallest, indicating that this sample consisted of smaller particles than the ones prepared from different starting materials (methods b and c).

SEM analysis of the differently prepared GaN samples confirmed the difference in size of the particles indicated by the Scherrer broadening[12] of the XRD pattern. GaN prepared by ammonolysis of Ga_2O_3 at 1000 °C had an average particle size of ~200 nm (Figure 2a). As could be seen under the SEM, most of these crystallites agglomerated to form rodlike structures that are on the order of 1 μm by 2−3 μm. The agglomerates seemed to be quite porous, as far as we were able to tell from the SEM pictures.

Figure 2b shows an SEM image of the GaN from the control experiment of preparing GaN by ammonolysis from Ga_2O_3 at 1100 °C. The higher reaction temperature did not change the porous appearance of the material. The smaller crystals are still clearly visible. The structure of the agglomerates had changed though. They did not display a uniform rodlike shape of a narrow size range anymore.

Samples prepared by methods b and c, on the other hand, showed larger crystals, most of which also exhibited a rodlike shape on the order of 1 μm by 1−3 μm. In addition, some larger particles of several micrometers were seen (Figure 3a,b). The crystals were also agglomerated and in some cases seemed to be fused together by neck formation (Figure 3a), but overall they appeared more solid than the porous material seen in Figure 2a,b.

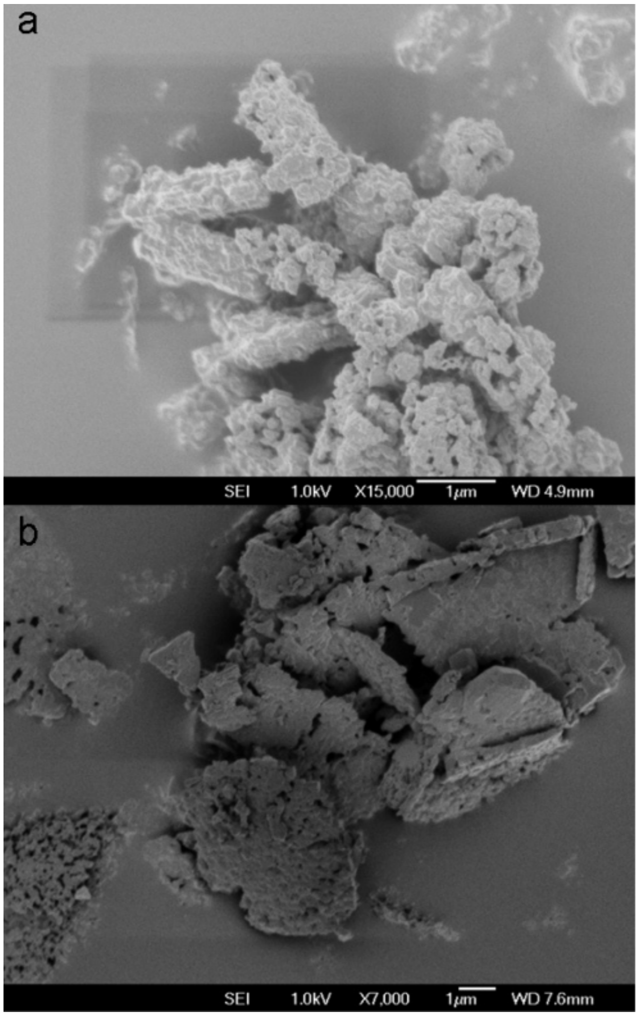

Figure 2. SEM image of GaN nanoparticles prepared by ammonolysis from Ga_2O_3 (a) at 1000 °C and (b) at 1100 °C.

We conclude that the difference in crystal size and shape between the three samples seen in Figures 2a and 3a,b were most likely due to the different starting materials used for the ammonolysis reaction, indicating that the initial shape and particle size of the starting material, starting from a powder compared to a metallic pellet, was retained in the product to a certain extent.

The optical properties of GaN particles synthesized from the different starting materials (Ga_2O_3, method a at 1000 °C; Ga_2O_3/Ga, method b at 1100 °C; and elemental Ga, method c at 1100 °C) were investigated by photoluminescence (PL) spectroscopy upon excitation with a He−Cd laser (325 nm, 300 K). The PL spectra of the different GaN materials are shown in Figure 4.

GaN prepared from Ga_2O_3 (Figure 4a) did not show any luminescence. The other two samples displayed intense band edge related luminescence at 374 nm (Figure 4b) and 378 nm (Figure 4c), respectively. The emission wavelength of sample c is somewhat longer than that observed for bulk GaN (373 nm[13]) but well within the range observed for other GaN nanostructures.[14] Neither of the samples showed any emission in the range of 500−650 nm. The absence of any yellow

---

[11] Rietveld refinements made use of version 1.23 of the XND Rietveld code: Birar, J.-F.; Garnier, P. *NIST Spec. Publ.* **1992**, *846*, 212.

[12] Hammond, G. S. *An introduction to crystallography and diffraction*; Oxford University Press: New York, 1998.

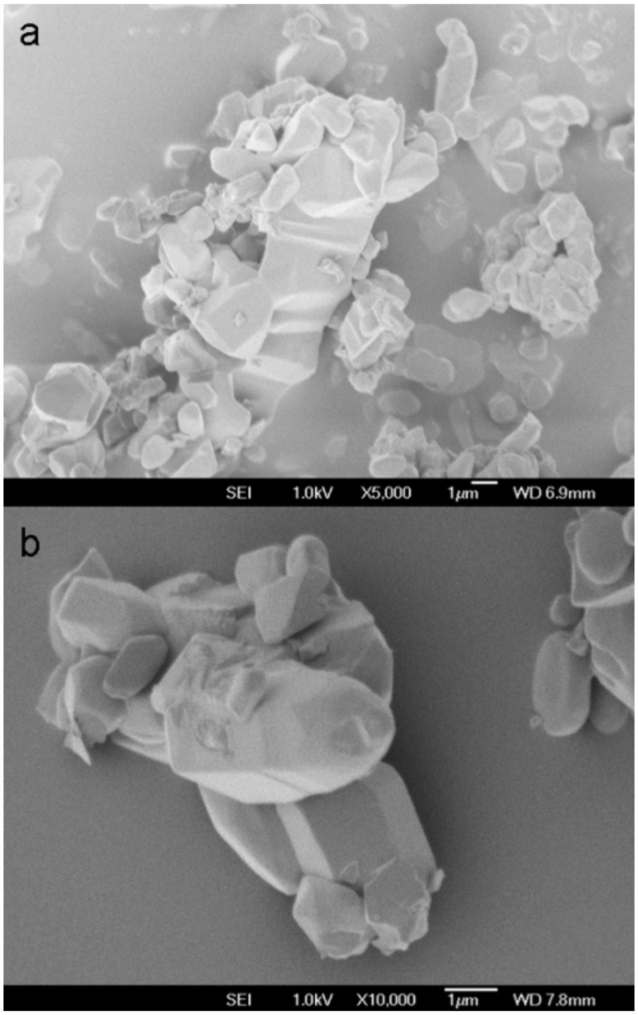

Figure 3. SEM image of GaN microstructures prepared by ammonolysis from (a) a mixture of Ga_2O_3/Ga and (b) elemental Ga.

emission can be interpreted as an indication that the samples do not have significant amounts of gallium vacancies.[15]

The ammonolysis of Ga_2O_3 has also been carried out at 1100 °C during this study. The intensity of the band edge related luminescence for those samples prepared at 1100 °C depended on the ammonia flow during the reaction (spectra not shown). For flow rates of ammonia higher than 30 sccm, no luminescence could be detected. Flow rates of ammonia lower than 30 sccm resulted in very weak band edge related luminescence. The intensity was not in any way comparable to the data seen in Figure 4b,c, and the maximum of the emission was located at 368 nm. If Ga_2O_3 was reacted with ammonia at 1000 °C, no luminescence was detected. This result was independent of the ammonia flow used.

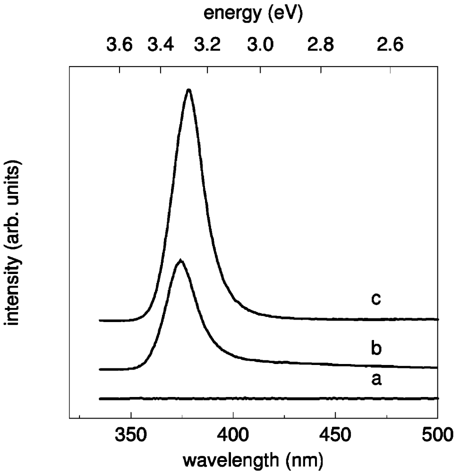

Figure 4. Photoluminescence spectra of GaN particles prepared by ammonolysis from (a) Ga_2O_3, (b) a mixture of Ga_2O_3 and metallic Ga, and (c) metallic Ga.

To further investigate which structural properties cause band edge related luminescence in GaN powders, we will discuss the differences in properties of three samples: a nonluminescing GaN sample prepared from Ga_2O_3 by ammonolysis at 1000 °C (method a) and a GaN samples prepared by method b from a mixture of Ga_2O_3/Ga and one sample prepared from metallic Ga (method c), the later two samples both being prepared at 1100 °C. The samples were investigated using solid-state ^1H and ^{71}Ga NMR. These analysis techniques allow us to detect deviations in the crystal structure of the materials on an atomic level. Especially the role of hydrogen impurities in GaN crystals with regard to the photoluminescence of the material is a frequent source of speculations, but to our knowledge, ^1H NMR experiments on GaN particles have not been conducted so far.

Figure 5 illustrates the two different types of ^1H MAS NMR spectra that were obtained from the GaN samples. As can be seen from the signal/noise ratio in the spectra, the overall amount of protons was considerably lower in Figure 5b, which represents a spectrum obtained from GaN prepared from elemental Ga (method c). The ^1H MAS NMR spectrum of GaN prepared by method b, from a Ga_2O_3/Ga mixture, was similar in appearance and intensity to the signals shown in Figure 5b (GaN prepared from elemental Ga (method c).

For GaN prepared by method a (Figure 5a), in addition to the signal for protons (~0 ppm), two sets of symmetric spinning sidebands could be detected. The presence of these spinning sidebands, coming from ^1H chemical shift anisotropy and/or H−H spin-pair homonuclear dipolar coupling, indicated that the protons were more or less solidly bound to their surroundings and could not rotate freely. Therefore, they have to be structural protons integrated into the crystal. For GaN prepared by method b or c, two proton signals were detected (Figure 5b). One of the proton signals showed the same chemical shift as the proton signal detected for the structural protons in Figure 5a. However, no spinning sidebands could be positively identified in the ^1H NMR spectrum due to the noise of the background. If structural protons were present in these samples, their quantity was very low. The other proton signal seen for GaN prepared from elemental Ga (method c) in Figure 5b is very sharp and showed no spinning sidebands, indicating that those protons present in the sample were either able to rotate freely and not structurally bound within the crystal or lack significant

---

(13) Kazlauskas, K.; Tamulaitis, G.; Zukauskas, A.; Prystawko, P.; Leszczynski, M.; Suski, T.; Perlin, P.; Gregory, I.; Porowski, *S. Phys. Stat. Sol. (c)* **2002**, 516.

(14) Gonsalves, K. E.; Rangarajan S. P.; Carlson, G.; Kumar, J.; Yang, K.; Benaissa, M.; José-Yacaman, M. *Appl. Phys. Lett.* **1997**, 71, 2175. Sardar, K.; Rao, C. N. R. *Adv. Mater.* **2004**, *16*, 425.

(15) Saarinen, K.; Seppälä, P.; Olia, J.; Hautojärvi, P.; Corbel, C.; Briot, O.; Aulombard, R. L. *Appl. Phys. Lett.* **1998**, *73*, 3253.

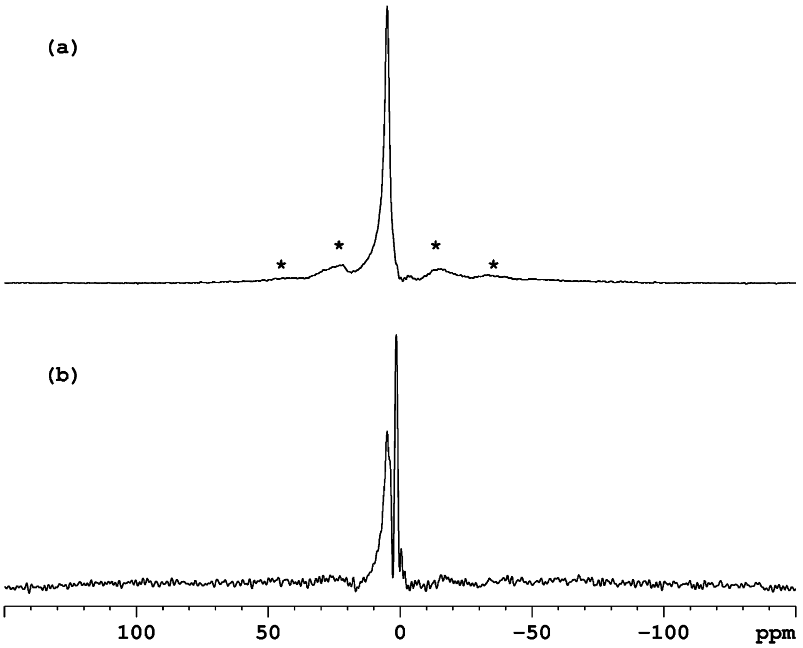

Figure 5. ^{1}H MAS NMR spectra of GaN (a) prepared by ammonolysis of Ga_2O_3 and (b) representative spectra of GaN prepared either from a mixture of Ga_2O_3 and metallic Ga or from metallic Ga alone. Note the presence of the spinning sidebands indicated by * in part a; spin rate of the sample 8000 Hz.

contribution from ^{1}H chemical shift anisotropy and/or pairwise homonuclear dipolar coupling.

^{71}Ga NMR gave unexpected results. The reported peak for pure GaN is observed around 330 ppm.[16] Previous publications showed reference data of commercially available GaN,[17] which in addition to this reported sharp peak showed some broad signal at lower field. Jung et al.[18] explain this broad signal with the presence of nitrogen-deficient GaN (GaN_{1-x} with $0 < x < 1$) in their GaN samples prepared from Ga_2S_3 by ammonolysis at temperatures higher than 800 °C.

Our GaN sample prepared from Ga_2O_3 (method a), showed only one narrow peak at 327 ppm (Figure 6a). The location of the peak as well as the sharpness of the signal confirmed the presence of GaN in the sample, which displayed a highly symmetric surrounding for the Ga atoms in the crystals, which would be given by highly stoichiometric GaN. This observation was in agreement with the study published by Jung,[19] who also reported only one peak in the ^{71}Ga NMR spectrum for the same reaction between 800 and 1000 °C.

Figure 6b shows the spectrum obtained for GaN prepared by method b. In addition to the sharp GaN peak at 327 ppm, a broad peak centered around 422 ppm with a shoulder around 385 ppm was observed. The broadening of these two overlapping signals may be attributed to a nonsymmetric environment for the Ga atoms and/or a chemical shift distribution, a reflection of the distribution of different Ga environments. The direction of the shift of these peaks downfield may indicate a nitrogen deficiency, as proposed by Jung et al.[18] Taking the area of the peaks as an indication of the amount of material of one type present in the sample, the presumably stoichiometric GaN (peak at 327 ppm) represented only a very small part of the sample. Concerning the ratio of the two nonstoichiometric GaN phases, it could only be assumed that the phase of GaN material with the peak centered around 422 ppm outweighs the amount of the other type of nonstoichiometric material, with a peak centered around 372 ppm.

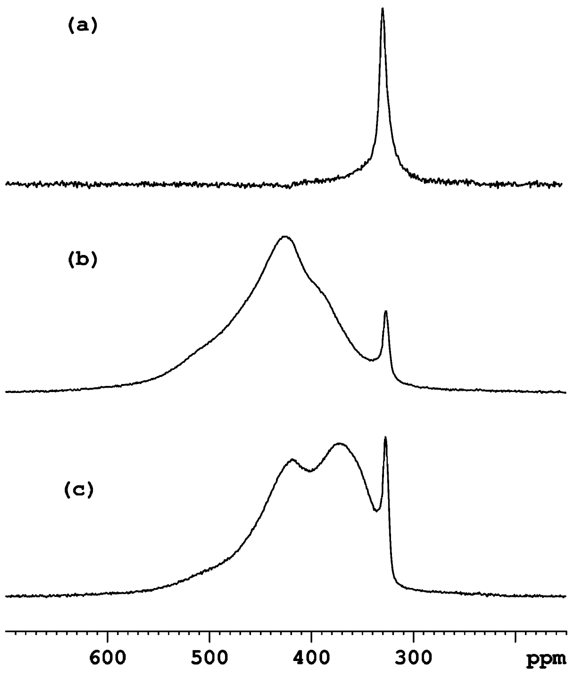

Figure 6. ^{71}Ga spin−echo NMR spectra of GaN prepared by ammonolysis (a) of Ga_2O_3, (b) of Ga_2O_3/Ga, and (c) of metallic Ga.

GaN prepared from metallic Ga (method c, Figure 6c) exhibited a sharp signal at 327 ppm corresponding to a stoichiometric ratio of Ga:N, according to literature

---

[16] Han, O. H.; Timken, H. K. C.; Oldfield, E. *J. Chem. Phys.* **1988**, *89*, 6046.

[17] Faulhaber, S.; Loeffler, L.; Hu, J.; Kroke, E.; Riedel, R.; Lange, F. F. *J. Mater. Res.* **2003**, *18*, 2350.

[18] Jung W.-S.; Park, C.; Han, S. *Bull. Korean Chem. Soc.* **2003**, *24*, 1011.

[19] Jung W.-S. *Mater. Lett.* **2002**, *57*, 110.

data, and two broad peaks at lower field. In this spectrum both of these peaks could be well-distinguished and were centered around 372 and 422 ppm, respectively.

In all the samples, no peak for metallic Ga was detected, even though for GaN prepared by method b or c a layer of metallic Ga was visible at the bottom of the alumina crucible at the end of the reaction.

In addition to the NMR studies, we obtained EDS data for the GaN samples prepared from Ga_2O_3 (method a) and from elemental Ga method (c). This was to probe the samples for oxygen incorporation, which could not be detected by the NMR experiments conducted during this study. For EDS analysis a rather large amount of sample is required, and we had to prepare the sample in multiple experiments. We refrained from testing GaN prepared from a mixture of Ga_2O_3 and metallic Ga, since we could not say for sure if the metallic Ga detected in the crucible after the reaction was due to unreacted starting material or a decomposition product of GaN. We did not deem it possible to prepare multiple samples by this method that have the same Ga_2O_3:Ga ratio down to a tenth of a millimole.

Analysis of GaN particles prepared from Ga_2O_3 (method a) gave a composition in atom percentage, with the standard deviation given in parentheses, of 52.3(3.1)% Ga, 41.8(2.2)% N, and 5.9(0.9)% O. The analysis results were quantified using a high-quality epitaxial GaN film grown on sapphire by MOCVD. The analysis indicates that the GaN particles are slightly nitrogen deficient. However, within the deviation, a stoichiometric ratio of Ga:(N and O) of 1:1 is obtained. The significant contamination of the material with oxygen is most likely due to unreacted residues of the starting material Ga_2O_3.

GaN prepared from metallic Ga by ammonolysis contains three different phases: one is beige-yellowish, like the material prepared by ammonolysis of Ga_2O_3 (method a) and contains 42.6% Ga, 54.5% N, and 2.9% O, as well as a nonquantified amount of carbon contamination (no deviations are given, since only selected spots of the sample were analyzed). Of the other two observed phases, one corresponds to almost stoichiometric GaN (49.6% Ga, 50.4% N) and the other one is strongly nitrogen-deficient (61.0% Ga, 39.0% N). Neither of the two phases contained measurable amounts of oxygen.

The determined Ga:N ratio in these three phases was not considered reliable enough for further analysis, since only one measurement was taken of each phase. Therefore, they will not be considered further in the following discussion of the obtained results. Since the difference in the detected oxygen content of the phases is significant, however, we will distinguish between one oxygen-containing and two oxygen-free phases for GaN prepared from elemental Ga (method c) throughout the rest of this publication.

Discussion

From all the analysis results accumulated, we can conclude the following structural differences for GaN prepared from Ga_2O_3 at 1000 °C (method a), which did not show any photoluminescence (Figure 4):

This GaN sample consisted of only one single phase of GaN according to its XRD pattern as well as the ^{71}Ga NMR spectrum. The observed homogeneous color and particle shape of the sample were in agreement with these findings. Furthermore, this was the only one of the three compared GaN samples that contained a significant amount of structurally bound protons (Figure 5a). In addition, no oxygen-free phase is present in this material according to EDS analysis, and the material is nitrogen-rich.

EDS analysis revealed the presence of significant amounts of oxygen in the sample prepared by ammonolysis from Ga_2O_3 (method a) as well as in the beige-yellowish phase of GaN prepared from elemental Ga (method c). It is known that oxygen in large amounts within epitaxially grown GaN layers suppresses luminescence in general. Since the oxygen content was high (5.9%) for GaN prepared from Ga_2O_3 (method a), this might be the reason no luminescence at all was detected for this sample. For GaN prepared by method c, which contains 2.9% oxygen in one phase, other phases were detected which showed no oxygen contamination; therefore, this is no help in determining if the suppressed luminescence in the sample prepared from Ga_2O_3 (method a) is due to the high oxygen content.

Furthermore, the EDS data showed that GaN prepared from Ga_2O_3 (method a) did not consist of GaN in a stoichiometric ratio of Ga:N; only after including the oxygen contamination was the ratio of Ga:(N + O) about 1:1. Judging from the sharpness of the signal observed by ^{71}Ga MAS NMR, highly stoichiometric GaN would have been expected, since a sharp peak in the ^{71}Ga MAS NMR spectrum is an indicator for high symmetry of Ga sites on the atomic level within the crystal. This highly symmetric environment for the Ga atoms in the crystal could in theory only be created if the atoms would be symmetrically surrounded by four nitrogen atoms as nearest neighbors in stoichiometric GaN. The coexistence of an oxygen-containing phase of unreacted starting material (Ga_2O_3) in the sample, which could explain the amount of oxygen detected by EDS, could not be supported by any of the analysis methods. No traces of unreacted Ga_2O_3 were found. It seems the occupation of some nitrogen sites with oxygen atoms indeed does not disturb the symmetry of nearest neighbors the Ga atom experiences within the crystal and a sharp signal is detected by ^{71}Ga NMR spectroscopy nevertheless.

In contrast to GaN prepared from Ga_2O_3 at 1000 °C, for both of the GaN samples that exhibited intense luminescence at room temperature, two additional signals were observed downfield in the ^{71}Ga NMR spectra (Figure 6b,c). These did not show the same sharpness as the previously discussed one but were very broad, indicating a nonsymmetric environment for the Ga nuclei and/or inhomogeneous broadening due to chemical shift distribution of Ga.

The general trend that within a group of similar Ga-containing compounds the chemical shift for Ga nuclei drifts to higher frequency (i.e. downfield) with the number of coordinated ligands decreasing[20] led us to the assumption that the peaks observed downfield with respect to GaN at 327 ppm correspond to Ga atoms not

---

(20) Bradley, S. M.; Howe, R. F.; Kydd, R. A. *Magn. Reson. Chem.* **1993**, *31*, 883.

coordinated to four neighboring nitrogen atoms as in the stoichiometric GaN (327 ppm) but that these observed Ga atoms were exhibiting decreased coordination numbers due to the nitrogen deficiency.

The two broad signals downfield are most likely due to different levels of beginning decomposition of GaN due to the high synthesis temperature. We assume the two different peaks at ~370 and 422 ppm represent Ga nuclei coordinated to only three and two N atoms, respectively. So far literature reports only mention the observation of one broad signal at higher frequency than the 327 ppm signal. The coexistence of three different phases in the material prepared from metallic Ga (method c) was also established visually and by EDS analysis. The XRD data for GaN prepared from metallic Ga (method c) showed two datasets, indicating hexagonal GaN (Figure 3c). The calculated lattice constants for both phases were surprisingly small for GaN. At this point we do not have an explanation for this reduction in cell size.

There also was the observed difference between the luminescing (methods b and c) and the nonluminescing (method a at 1000 °C) GaN samples that GaN prepared from Ga_2O_3 (method a) contained a significant amount of structurally bound protons within the crystal (Figure 5a), while for the other samples very few possibly structurally bound protons and in addition surface absorped protons could be exhibited. Protons bound to the surface of the crystal should be able to rotate unhindered in the case of these particles, since no capping agents were used to passivate the surface of the GaN. Therefore, we are assuming that we are seeing surface protons, most likely from either H_2O absorbed on the surface after the preparation of the material or from protons bound to the surface by coordinatively unsaturated nitrogen atoms, resulting from the synthesis method used. It could not be ruled out that GaN prepared from Ga_2O_3 also contains surface protons, since the signal for structurally bound protons and the one for surface protons appear in the same region of the spectrum and would overlap if the signal for structurally bound protons was intensive enough. Considering that the same general method of preparation was used for all samples, i.e., using ammonia as the nitrogen source, it is very likely that this sample also contains protons bound to the surface of the particles.

To support our assumption of a correlation between the additional features in the ^{71}Ga NMR of GaN prepared from Ga_2O_3/Ga (method b) and metallic Ga (method c), indicating nitrogen-deficient phases in the crystal and the observation of band edge related luminescence, the following experiment was carried out:

GaN prepared from Ga_2O_3 (method a) was heated to 1100 °C under a constant flow of nitrogen and kept at this temperature for 30 min. Epitaxial layers of GaN are known to decompose under nitrogen loss at elevated temperatures. If the two additional signals seen in the ^{71}Ga NMR are indeed due to nitrogen-deficient phases, they should be detectable at the end of this experiment. While the starting material was beige-yellow in color, the content of the crucible was metallic gray when the alumina boat was removed from the furnace, indicating a beginning decomposition of the material. When examining the material in more detail, it was found that the lowest layer of material in the crucible was still beige-yellow; only the material on the surface, which was directly exposed to the nitrogen flow, had reacted, i.e., started to decompose. Indeed metallic Ga was present in the sample and prevented the sample from spinning in the MAS experiments. So we were only able to obtain a static ^{1}H NMR as well as static ^{71}Ga NMR of the sample, while the previously mentioned data was obtained by MAS NMR with spinning rates of 8000 Hz (^{1}H MAS NMR) and 14 000 Hz (^{71}Ga MAS NMR). Due to these experimental limitations, we can only conclude that protons are present in the system, but we are not able to distinguish between structurally bound protons and protons absorbed on the surface of the particles.

The ^{71}Ga NMR spectrum was similar to the data of a static Hahn−Echo experiment of GaN prepared from elemental Ga (spectra not shown). In both these spectra a NMR signal downfield of GaN at 327 ppm was observed. The resolution in static experiments is not as high as for spinning MAS experiments; therefore, no two peaks can be distinguished. Instead, one broad feature was exhibited. From the knowledge gained by the spinning MAS NMR spectra of GaN obtained from Ga_2O_3/Ga (method b) and metallic Ga (method c), we can conclude that the broad feature seen in the static ^{71}Ga NMR of the GaN annealed under nitrogen is due to nitrogen-deficient phases. These phases were introduced by the annealing process, which is another indication that they are indeed due to beginning decomposition of GaN.

When the annealed powder was excited with a He−Cd laser (325 nm, 300 K), band edge related luminescence centered at 368 nm was observed. The peak had a broader width at half-maximum, but it is still one distinct peak. The same wavelength was observed for GaN prepared from Ga_2O_3 that was reacted with ammonia at 1100 °C and an ammonia flow of 20 sccm. Again, no other emission at longer wavelengths could be detected.

This observation strengthened the theory that the introduction of nitrogen deficiencies into the GaN is either directly or indirectly (no oxygen contamination, no structural protons) linked to the observation of band edge related luminescence in GaN particles.

For GaN prepared from Ga_2O_3 ammonia at 1100 °C and with an ammonia flow of 20 sccm, a ^{1}H NMR spectrum was recorded. It showed no evidence of structural protons. This further strengthens the role structural protons play in the sample, since all samples we looked at displayed band edge related emission unless structural protons could be detected in the sample.

To clarify whether nitrogen deficiencies are the cause of photoluminescence in GaN powders and whether structural protons quench the luminescence in GaN particles, further investigations are in progress.

Conclusion

We were able to show that structural and optical properties of GaN powders strongly depend on the choice of Ga-containing starting material if the GaN crystals are synthesized by ammonolysis. The differently prepared GaN samples revealed a strong correlation between two different types of nitrogen deficiencies and the presence of structural protons, both detected by NMR spectroscopy, and the band edge related photoluminescence observed for the material. From the results of this work, we are confident that the band edge related luminescence in GaN powders is either directly or indirectly (no oxygen contamination, no structural protons) linked to the observation of nitrogen-deficient phases in the ^{71}Ga NMR spectrum of the material prepared from Ga_2O_3/Ga (method b) or metallic Ga (method c).

^{71}Ga NMR is a very useful tool for determining the properties of GaN, and different phases can be determined more reliably than by XRD. In addition, ^{1}H NMR spectroscopy is one of the few tools by which hydrogen impurities in GaN can actually be tracked down and one can differentiate between surface adsorbed protons and structurally bound ones.

Acknowledgment. This research was supported by the Solid State Lighting and Display Center at UCSB. This work made use of MRL Central Facilities supported by the MRSEC Program of the National Science Foundation under award No. DMR00-80034. We also thank Frederick F. Lange for his support.

CM049094S