Aerosol-Assisted Vapor Phase Synthesis of Gallium Nitride Powder

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During the last 10 years, gallium nitride (GaN) has received much attention due to its band gap,[3] electroluminescent,[3−5] and photocatalytic[6] properties that make the material potentially useful in high-temperature electronic, optoelectronic, and fuel cell applications. The need for pure and morphologically well-defined material has stimulated development of new synthetic methodologies for GaN, and several recent reports have reviewed the available approaches for preparing thin films,[7−9] single crystals,[10] nanocrystals,[11−15] quantum dots,[16,17] nanowires,[18] and nanorods.[19] The somewhat exotic yet desirable advanced forms are typically obtained by using elaborate preparative equipment and/or expensive, air-sensitive molecular precursor chemistry that tend to limit large-scale materials development and increase application costs. On the other hand, polycrystalline GaN powders can be prepared by several straightforward methods that include heating (1000 °C) Ga/Li in $NH_3(g)$,[20] heating (>900 °C) Ga metal, Ga_2O_3, or Ga halides in $NH_3(g)$,[21] and igniting mixtures of $GaI_3/NH_4Cl/Li_3N$[22] in a closed system. Balkas and Davis[21] have reexamined the pertinent thermodynamics of elementary reactions, and they conclude that both Ga metal and Ga_2O from Ga_2O_3, with $NH_3(g)$ should efficiently serve as chemical feedstocks for the production of submicrometer h-GaN powder.[21]

Aerosol-based syntheses[23,24] provide potentially simple, economic methods for preparing nonoxide ceramic powders with excellent control over purity and particle morphology. Our successes in generating large samples (>2 g/h) of submicrometer h-BN[25] and AlN[26] powders with a laboratory scale aerosol-assisted vapor phase synthesis (AAVS) reactor using cheap, readily available, and pure precursors, e.g., aqueous solutions of H_3BO_3 and $Al(NO_3)_3$, have led us to evaluate the AAVS method for GaN production. Neither gallium metal nor gallium oxides can be easily employed in an AAVS reactor; however, aqueous soluble gallium salts should be useable. We communicate here our initial advances in preparing h-GaN powders by using two-step AAVS nitridation chemistry that employs aqueous $Ga(NO_3)_3$ and $NH_3(g)$ as starting materials. The validity of this approach is supported by a report[27] that appeared during the preparation of this paper on the conversion of $Ga(NO_3)_3$ to nanocrystalline h-GaN in a sol−gel prepared silica matrix.

An aqueous solution, prepared with $Ga(NO_3)_3 \cdot xH_2O$ (13.6 g in 250 mL of distilled water), is placed in a glass tube (4.5 cm × 22.70 cm) that is closed at the bottom with a thin polyethylene bottle cap. The top of the tube is reduced in diameter (1.3 cm) and connected through a short section of Tygon tubing to a stainless steel end cap on a horizontal mullite tube (3.5 in. o.d. × 60 in.) that rests in a Lindberg three-zone tube furnace held at 1050 °C (36 in. hot zone). An aerosol mist of the $Ga(NO_3)_3$ solution is generated by placing the polyethylene capped tube end over an ultrasonic transducer operating at 1.7 kHz. In initial experiments, $N_2(g)$ (5.2 L/min) is injected into the aerosol mist generator through a sidearm placed about 1 in. above the solution surface. The aerosol is swept through the connecting Tygon tubing into the heated mullite reaction tube by the stream of $N_2(g)$ (5.2 L/min). Under these conditions, the estimated residence time in the furnace hot zone is 12 s. The exit of the reactor tube is connected to an assembly containing a nylon impact filter from which product powder is harvested. The aqueous mist containing $Ga(NO_3)_3$ initially dries and then reacts producing a white powder with spherical morphology as shown by scanning electron microscopy (SEM). The majority of

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particles are smaller than 0.5 μm. A powder X-ray diffraction (XRD) scan reveals that the particles are crystalline, and the XRD pattern agrees with that obtained from an authentic sample of Ga_2O_3.[28] The decomposition of $Ga(NO_3)_3$ to Ga_2O_3 in flowing N_2(g) is consistent with literature reports.[29,30]

Injection of NH_3(g) (N_2, 3L/min; NH_3, 99.5%, 2.2 L/min) into the aerosol stream results in the formation of a pale yellow powder. Bulk chemical analysis (CGaHNO)[31] of the powder suggests a composition $Ga_{2.19}H_{1.75}N_{1.00}O_{2.49}$, and this powder is referred to hereafter as GaN_xO_y. The analyses show absence of carbon. The observation of only partial nitridation is a consequence of the short residence time (~12 s) in the reactor. When the reactor is held at slightly higher temperature (1100 °C), the x/y ratio changes from 0.4 to 0.5.[32] Energy-dispersive X-ray analysis (EDX) scans contain Ga peaks (1.19, 9.22, 10.39 keV), a nitrogen peak (0.39 keV), an oxygen peak (0.52 eV), and a very faint Si peak (1.84 keV). The partially nitrided GaN_xO_y has a density of 4.41 g/cm^3 and a surface area of 11.5 m^2/g. The powder XRD displays broad diffuse reflections at $2\theta = 28°-40°$, $45°-50°$, $56°-60°$, $62°-66°$. The SEM (Figure 1) for this partially nitrided powder indicates that the particles are spherical, but they have some surface texture or "cauliflowering". The average particle size is still less than 0.5 μm.

To complete the nitridation, a sample of GaN_xO_y (0.706 g) is placed in an alumina crucible and heated (1050 °C, 5 h) under a flowing stream (0.5 L/min) of NH_3(g). The resulting powder (0.608 g)[33] is yellow and gives chemical analysis data[31] that are in close agreement with GaN. The measured density and surface area are 6.28 g/cm^3 and 3.34 m^2/g, respectively. The EDX scans for this powder show Ga and N peaks and a very low intensity peak for oxygen. The powder XRD for the product agrees nicely with the data reported by Balkas and Davis for phase pure h-GaN.[21] A SEM (Figure 2) for this powder indicates that some of the particles are loosely agglomerated and the agglomerates are composed of sharply faceted particles, 0.1−0.5 μm in size. The sample also contains many unagglomerated particles. Transmission electron micrographs (TEM) for the sample further reveal that the agglomerates contain a range of crystallite sizes (20−200 nm), and the unagglomerated particles are mostly in the 20−50 nm size range. Selected area electron diffraction (SAED) shows that the large, well-formed crystals display the expected hexagonal symmetry diffraction pattern while the agglomerated nanocrystalline particles produce diffraction ring patterns that are indexed in agreement with the GaN hexagonal lattice.[34]

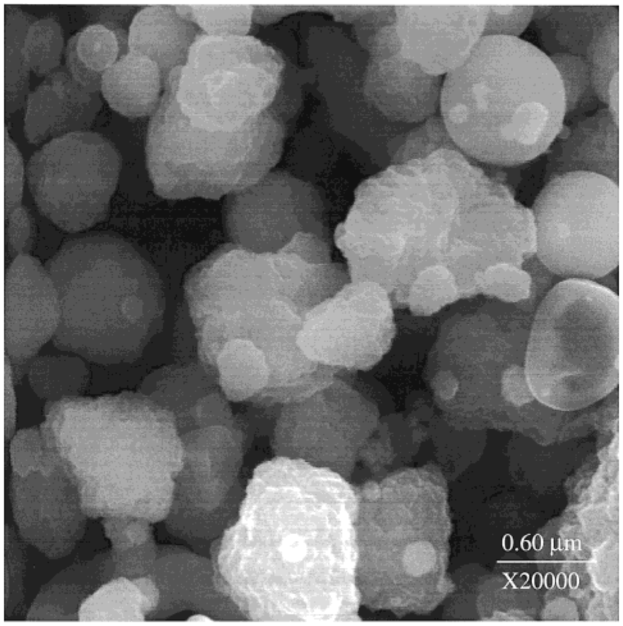

Figure 1. SEM of GaN_xO_y aerosol particles produced at 1050 °C.

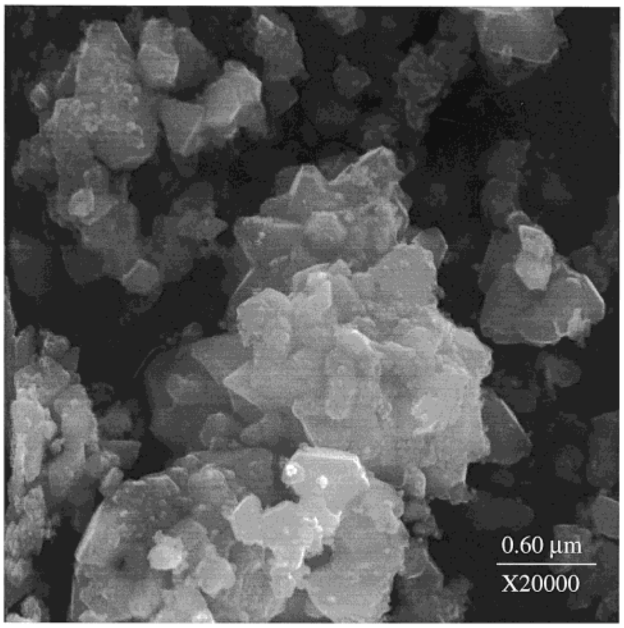

Figure 2. SEM of GaN aerosol particles.

The collected data are fully consistent with the formation of phase pure h-GaN from an easily accomplished two-stage AAVS nitridation process that employs air-stable aqueous solutions of $Ga(NO_3)_3$. The

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(28) Comparative XRD data are from the International Center for Diffraction Data (ICDD) Powder Diffraction Files (PDF): http://www.icdd.com.

(29) A thermogravametric analysis (TGA) scan (10 °C/min under N_2) for $Ga(NO_3)_3 \cdot xH_2O$ used in these experiments shows a significant weight loss (~65%) between 40 and 200 °C. An additional 10% loss occurs between 200 and 400 °C. The hydration number x is not specifically stated by the commercial supplier; however, the sample melts between 65 and 70 °C as reported for samples with $x = 9$.[30] If $x = 9$ and Ga_2O_3 is formed during the TGA scan, the expected weight loss would be 55.1% according to the equation: $2Ga(NO_3)_3 \cdot 9H_2O \rightarrow Ga_2O_3 + 15H_2O + 6HNO_3$. Conversion to Ga_2O would result in additional weight loss (62.8%). It should be noted that the thermal rise time in the TGA scan (4°C/min, 50−1100°) is much slower than that in the AAVS experiment, and this certainly impacts the parallel rates of aerosol drying, Ga(III) hydrolysis, and gallium oxohydroxide nitridation.

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(31) The C Ga HN analyses were performed in duplicate by the Laboratory for Microanalysis, Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia. The oxygen analyses were performed at Advanced Ceramics Corp., Lakewood, OH. Aerosol powder (GaN_xO_y) (observed): C, 0.00; Ga, 72.36; H, 0.90; N, 7.16; O, 20.36. Annealed powder (observed): C, 0.00; Ga, 83.28; H, 0.00; N, 16.78; O, 0.90. Calcd: GaN Ga, 83.27; N, 16.73.

(32) Three samples, prepared under different reactor conditions, were analyzed for composition, and the data varied slightly in the N/O ratio as a function of $Ga(NO_3)_3$ solution concentration and reactor temperature.

(33) Using the composition provided by the bulk chemical analysis, the theoretical nitridation yield for this sample should be 0.621 g.

AAVS chemistry is no doubt complex, but it appears to involve initial drying of the aqueous aerosol droplets followed by decomposition of the $Ga(NO_3)_3$ into spherical morphology gallium oxide particles. In parallel with this chemistry, nitridation of the gallium oxide with NH_3 and/or its cracking products, NH_2, NH, and H, occurs. On a molecular level, the aqua−Ga(III) ion probably undergoes rapid initial hydrolysis forming spherical oxohydroxide particles that undergo the nitridation chemistry; however, this is not unambiguously demonstrated. The rates for the parallel hydrolysis and nitridation processes are likely well balanced as the spherical particle morphology is retained until nitridation is nearly complete. In the final step, GaN crystallization and densification occurs giving the observed nanocrystals, nanocrystal agglomerates, and micrometer-sized single crystals. Further work, will be required to define a larger scale, single-step AAVS process that directly produces high-purity h-GaN powder with lower levels of residual oxygen. It should be economically feasible to achieve this goal. It should also be possible to gain process control over the GaN_xO_y polydispersity and subsequent nanocrystal growth and agglomeration such that more narrow particle size distributions are realized.

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Supporting Information Available: Thermogravametric analysis scans for $Ga(NO_3)_3{\cdot}xH_2O$, XRD scans and SEM for its oxide decomposition product, EDX and XRD data for GaN_xO_y, and XRD, TEM, and SAED data for GaN powders. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) The SAED patterns from large (0.5−1.5 μm) single crystals index in full agreement with the wurtzitic hexagonal GaN structure. Views from [100] and [001] planes are provided in Supporting Information. The SAED pattern obtained from nanocrystal agglomerates appears as a powder pattern that also indexes as h-GaN.