Tuning aerosol-assisted vapor phase processing towards low oxygen GaN powders

J. F. Janik[*, 1], **M. Drygaś**[1], **S. Stelmakh**[2], **E. Grzanka**[2], **B. Pałosz**[2], and **R. T. Paine**[3]

[1] AGH University of Science and Technology, Faculty of Fuels and Energy, Kraków, Poland
[2] Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw, Poland
[3] University of New Mexico, Department of Chemistry, Albuquerque, NM, USA

Herein, are reported studies of various experimental conditions aimed at optimizing the Aerosol-Assisted Vapor Phase Synthesis (AAVS) of GaN powders. In general, the process utilizes affordable oxygen-bearing gallium precursors in aqueous/methanol solutions to initially prepare nano-sized GaN_xO_y powders of spheroidal morphology. Subsequent pyrolysis of the GaN_xO_y intermediate in a NH_3 atmosphere converts the powders to sub-micron, crystalline GaN powders that usually contain some residual oxygen. The application of appropriate solvents, *e.g.*, methanol, in the aerosol powder generation stage and the use of pyrolysis temperatures in the range 900–1000 °C may improve both the extent of nitridation and, to certain degree, the control over average particle sizes. The characteristics of the AAVS-produced materials are compared with those for bulk GaN powders obtained by direct nitridation of commercial gallium oxide.

1 Introduction

Gallium nitride GaN is of vital scientific and commercial interest for various material applications in advanced electronic devices. It appears that the use of GaN-based film structures in efficient low-wavelength light emitting devices has been a major driving force for numerous attempts to refine the synthesis and to improve performance characteristics [1–5]. Among the synthetic approaches used, results obtained from bulk powder syntheses of oxygen-free [6–11] or low-oxygen [12–17] GaN/GaN-based powders have contributed to a better understanding of the properties while offering new, exciting and affordable applications. Potential application areas include, but are not limited to photonic crystals [18] and quantum dots in optoelectronics [5, 19], powder sublimation sources for growth of GaN layers [20], spintronic materials [13, 21] and, upon compacting/sintering alternative wafer supports for growing light-emitting heterostructures [6].

Commercially available oxygen-bearing gallium compounds seem to constitute the most affordable pool of precursors for GaN powders. However, such compounds when used in standard powder syntheses are characteristic of persistent residual oxygen contents. This vicious problem in efficient conversion/nitriding of such precursor systems to bulk GaN powders, usually under reactive ammonia atmosphere, is associated with the necessity to use high reaction temperatures (900–1100 °C) for prolonged times due to slow, diffusion controlled Ga–O to Ga–N reactions. This also happens to be the range of thermal stability of GaN. Hence, this processing may result in non-stoichiometric compositions (N-deficiency), concurrent decomposition with Ga metal formation, partial resublimation, and/or residual oxygen contents. Often, all of these appear at once.

* Corresponding author: e-mail: janikj@agh.edu.pl, Phone/Fax: +(48) (12) 617 2577

The convenient Aerosol-Assisted Vapor Phase Synthesis (AAVS) of GaN powder also utilizes commercial oxygen-bearing gallium compounds, *e.g.*, gallium nitrate, soluble in water [17] or methanol [13]. In this process, complex decomposition and nitridation reactions take place during the aerosol generation stage between ammonia and submicron-sized droplets containing the gallium precursor and solvent. The reactions occur with relatively short residence times (10−60 s) in the reactor hot zone. The powders obtained from this first stage, labeled GaN_xO_y, may contain significant quantities of oxygen and they contain nanocrystalline GaN domains and some unreacted gallium oxide. These powders are then subjected to a follow-up pyrolysis under ammonia that gives prevailingly hexagonal GaN (h-GaN) materials containing some residual oxygen. Herein, several conditions for both the aerosol powder generation stage and subsequent nitriding pyrolysis are presented and discussed from a viewpoint of residual oxygen content and crystalline and morphological features of the resulting h-GaN powders.

2 Experimental

Ga_2O_3 was purchased from Aldrich (+99.99%) and was used to prepare gallium nitrate *via* dissolution in hot, concentrated nitric acid. Generation of GaN_xO_y aerosol powders (NH_3 flow = 3 L/min, N_2 flow = 1 L/min, mullite tube reactor) and subsequent pyrolysis experiments (alumina or BN boat-shaped crucibles, 6 hours, NH_3 flow = 0.5 L/min) were carried out according to the published procedures using gallium nitrate solutions of approx. 0.13 M (less conc.) or 0.26 M (more conc.) *vs.* Ga^{+3} [13, 17]. Some aerosol generations were executed under an exclusive nitrogen atmosphere to yield Ga_2O_3 aerosol powders. Oxygen analyses reported here as O-contents were provided by GE Advanced Ceramics (GE AC), Strongsville, OH, USA, and by Saint−Gobain Advanced Ceramics Corp. (S−G ACC), Amherst, NY, USA. *Note, we have found that O-analyses for low oxygen contents (below 2 wt%) derived by GE Advanced Ceramics tend to be on average higher compared with values for similar samples analyzed by Saint−Gobain Advanced Ceramics Corp.* XRD scans for product powders were obtained with a Siemens D5000 diffractometer using Cu K_α source. Average crystallite sizes for GaN were determined with the Scherrer' equation [22]. SEM images were acquired with a Hitachi S-800 scanning electron microscope for palladium/gold coated samples.

3 Results

Table 1 contains selected analytical data for the GaN_xO_y aerosol powders generated at 1100 °C from aqueous solutions and for pyrolyzed product powders (alumina crucible) in the range 900−1000 °C.

Table 1 Analytical data for GaN powders prepared from GaN_xO_y powders obtained from 1100 °C-generated aqueous aerosols (n/d – not detected; * – phase at the limits of detection).

1100 °C-generated aerosol; 0.26 M solutions; O-contents in the 11−14 wt% range				
XRD	mostly nano-h-GaN, av. size, 12 nm; some nano-monoclinic Ga_2O_3			
	pyrolysis temperature (alumina crucible)			
	900 °C	950 °C	975 °C	1000 °C
weight loss during pyrolysis, wt%	8.8−9.5	13.3	17.7	23.6
O-content, wt% (GE AC)	4.4−4.5	2.9	2.1	2.0
XRD: major phase	h-GaN	h-GaN	h-GaN	h-GaN
minor phase	n/d	Ga_2O_3*	Ga_2O_3*	n/d
GaN av. size, nm	12−13	14	19	18

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Tables 2 and 3 present similar data for GaN_xO_y powders generated at 1050 °C and 1000 °C, respectively, from aqueous solutions and for pyrolyzed powders (alumina and BN crucibles) under the same conditions as above. Note that some samples were first pyrolyzed at a lower temperature, typically below 950 °C and, subsequently, pyrolyzed again at a higher temperature to improve nitridation progress (2-stage).

Table 2 Analytical data for GaN powders prepared from GaN_xO_y powders obtained from 1050 °C-generated aqueous aerosols (* – phase at the limits of detection).

1050 °C-generated aerosol; 0.26 M solutions; O-contents in the 13–19 wt% range							
XRD	nano-h-GaN, nano-monoclinic Ga_2O_3						
	pyrolysis temperature						
	800 °C	900 °C	950 °C	950 °C 2-stage a) 800 °C b) 950 °C	950 °C 2-stage a) 900 °C b) 950 °C	975 °C	975 °C	1000 °C
	alumina crucible					BN crucible		
weight loss during pyrolysis, wt%	4.4	10.6	19.0	11.7	13.5	17.8–22.0	19.4–22.0	24.0
O-content, wt% (S–G ACC)	–	6.3	1.4	1.8	2.5	1.9–2.3 (GE AC)	1.8–2.0	1.5
XRD: major phase	–	–	h-GaN	–	–	h-GaN	h-GaN	h-GaN
minor phase			Ga_2O_3*			Ga_2O_3*	Ga_2O_3*	Ga_2O_3*
GaN av. size, nm			18			17	23	26

Table 3 Analytical data for GaN powders prepared from GaN_xO_y powders obtained from 1000 °C-generated aqueous aerosols (* – monoclinic phase in significant quantity).

1000 °C-generated aerosol; 0.13 M solutions; O-contents not available				
	pyrolysis temperature (alumina crucible)			
	800 °C	900 °C	950 °C 2-stage a) 800 °C b) 950 °C	950 °C 2-stage a) 900 °C b) 950 °C	1000 °C
weight loss during pyrolysis, wt%	3.8	6.7	13.2	10.9	25–32
O-content, wt% (S–G ACC)	15.2	8.9	1.8	–	0.4–0.8
XRD: major phase	–	h-GaN	–	–	–
minor phase		Ga_2O_3*			
GaN av. size, nm		17			

Table 4 Analytical data for GaN powders obtained from methanol solution 1050 °C-generated GaN$_x$O$_y$ aerosol powders (* – phase at the limits of detection).

1050 °C-generated aerosol; 0.13 M solutions; O-contents in the 19.4−20.2 wt% range		
	solution in mixture H$_2$O/CH$_3$OH = 5/1 (vol.)	solution in neat CH$_3$OH
XRD	nano-GaN, urea	–
	pyrolysis temperature (BN crucible)	
	975 °C	1000 °C
weight loss during pyrolysis, wt%	39.7	9.6
O-content, wt% (S−G ACC)	2.0	1.0
XRD: major phase minor phase GaN av. size, nm	h-GaN Ga$_2$O$_3$* 21	–

Table 4 above includes the data for aerosol powders generated from water-methanol or neat methanol solutions. The final pyrolysis experiments were done in BN crucibles. These systems were plagued by low yields of dark to black, sticky aerosol powders. Due to the their sticky, sooty nature significant quantities of the powders were retained in the reactor tube.

Table 5 Analytical data for GaN powders obtained from nitridation of commercial Ga$_2$O$_3$ and from 1050 °C-generated under nitrogen atmosphere Ga$_2$O$_3$ aerosol powder (n/d – not detected; * – phase at the limits of detection; ** – monoclinic phase in significant quantity).

	1050 °C-generated Ga$_2$O$_3$ aerosol under N$_2$			commercial Ga$_2$O$_3$			
	calculated O-content in pure Ga$_2$O$_3$, 25.6 wt%						
XRD	monoclinic Ga$_2$O$_3$ av. size, 29 nm			–			
	pyrolysis temperature						
	950 °C	975 °C	975 °C 2-stage a) 950 °C b) 975 °C	1000 °C	900 °C	950 °C	975 °C
	alumina crucible			BN crucible			
weight loss during pyrolysis, wt%	16.7	31.9	24.2	33.7	11.9	27.8	28.8
O-content, wt%	10.7 (GE AC) sintered	3.8 (GE AC) sintered	4.5 (GE AC) sintered	0.1 (S−G ACC) agglom.	4.2 (S−G ACC) agglom.	1.7 (S−G ACC) agglom.	1.3 (S−G ACC) agglom.
XRD: major phase minor phase GaN av. size, nm	h-GaN Ga$_2$O$_3$** 19	h-GaN Ga$_2$O$_3$* 22	h-GaN Ga$_2$O$_3$** 22	h-GaN n/d 47	h-GaN n/d 16	h-GaN Ga$_2$O$_3$* 22	h-GaN Ga$_2$O$_3$* 30

Table 5 contains the results obtained from direct nitridation with ammonia of commercial and aerosol generated gallium oxides. The pyrolysis under ammonia of the aerosol generated Ga_2O_3 resulted in sintered bodies that required grinding before sampling. Comparable products obtained from commercial Ga_2O_3/NH_3 were only slightly agglomerated on top layers in the crucible.

4 Discussion

From Tables 1 and 2, it appears that use of a slightly higher aerosol reaction temperature (1100 °C) results in lower average oxygen contents in the initial GaN_xO_y aerosol powders. However, this trend does not converge to lower oxygen contents in the products after the subsequent pyrolysis at 950–1000 °C. In this regard, in most systems these pyrolysis temperatures consistently resulted in 1–2 wt% residual oxygen contents in the GaN powders independent of the earlier aerosol generation history. The lowest O-contents equal to or below 1 wt% were found after the 1000 °C pyrolysis (see, Tables 3–5). It is obvious that under the conditions used in this study (pyrolysis time, ammonia flow, types of crucible), pyrolysis below 950 °C yields products containing significant amounts of oxygen. This oxygen is prevailingly in the form of monoclinic Ga_2O_3 – the preferred phase of gallium oxide as corroborated by XRD results (*vide infra*). Even using methanol as the aerosol precursor solvent that might facilitate nitridation of the Ga–O bond *via* carbothermal reduction/nitridation mechanism the residual oxygen contents still remained in the 1–2 wt% range (Table 4). Interestingly, urea was found in one first stage aerosol sample and its presence/volatility was likely associated with the high weight loss during the final pyrolysis stage (Table 4).

Higher O-contents were found in the products after a 2-stage final pyrolysis compared to a single stage at the same final temperature, *i.e.*, at 950 °C (Table 2) and 975 °C (Table 5). It appears that the partial/inefficient nitriding pyrolysis at temperatures below 950 °C was detrimental to the additional pyrolysis at a higher temperature from a point of view of residual oxygen contents. This may result from recrystallization of the oxide and its encapsulation by a GaN surface shell in the first pyrolysis stage. This in turn would prevent and/or slow down efficient nitridation by ammonia in the second stage at slightly higher temperatures.

The XRD data strongly indicate that hexagonal GaN is the only crystalline phase of gallium nitride formed in these systems under all probed conditions. This is contrary, for example, to the anaerobic routes to nanocrystalline GaN *via* conversion of gallium imide [23–25] or cyclotrigalazane [26, 27] where some cubic GaN and/or defected hexagonal GaN phases are formed at pyrolysis temperatures below 800–900 °C.

In the majority of samples that contained sufficient gallium oxide component, the patterns after indexing h-GaN could be assigned to monoclinic Ga_2O_3 (JCPDS No. 43-1012). Generally, for the products pyrolyzed at 975–1000 °C (and for some even at 950 °C), the amounts of Ga_2O_3 were on the verge of detection by XRD (Tables 1–5) and peak deconvolution techniques were used to prove the presence of the oxide. This fact is consistent with the low levels of O-contents determined by chemical analysis of the powders. In some powders, no oxide was detected using this approach. The source of this observation could be twofold. First, for the materials pyrolyzed at 900 °C or below and for the aerosol powders generated under an ammonia flow, the diffraction peaks are very broad and overlapping (v. small crystalline domains). The relatively broad and weak peaks for the oxide could not be detected within the noise level despite significant oxygen contents. Second, the absence of such diffractions for the powders pyrolyzed at 1000 °C that otherwise displayed sharp peaks was due to low contents of Ga_2O_3 below detection limits of the method.

The average crystallite size data derived from the Scherrer' equation indicate that nanocrystalline h-GaN is already formed during the initial aerosol generation stage (Tables 1 and 2). The application of the subsequent nitriding pyrolysis in the range 950–1000 °C results in increased quantities of GaN with average crystallite sizes depending on pyrolysis temperature and ranging from 14 nm at 900 °C to 47 nm at 1000 °C. In this regard, SEM images acquired for many of these powders (not shown here) support the presence of numerous very large GaN crystallites with sizes exceeding 100 nm especially after the 975–

1000 °C pyrolyses. Generally, the use of aqueous [13, 17] and methanol solutions [6] provides product powders with different spheroidal morphologies.

The application of the highest pyrolysis temperatures at 975–1000 °C was associated with significant sublimation and decomposition phenomena. In some cases, metallic gallium could be identified on the bottom and long needles of resublimed GaN were observed grown on the rim of the crucible. These phenomena account for the relatively large weight losses in such cases exceeding the 10.7% theoretical weight loss for the complete Ga_2O_3 to GaN conversion.

5 Conclusion

Nanocrystalline h-GaN powders with different spheroidal morphologies and average crystallite sizes below 50 nm can be conveniently obtained from affordable precursors by the application of the Aerosol-Assisted Vapor Phase Synthesis from aqueous and methanol solutions. These powders typically contain residual oxygen in the range 1–2 wt%. However, it is possible to choose experimental conditions to reach O-contents as low as a few tenths wt%.

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