Ammonothermal Synthesis of Cubic Gallium Nitride

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The metastable cubic (zinc blende) form of gallium-(III) nitride (c-GaN) has been grown heteroepitaxially on lattice matched substrates such as β-SiC, GaAs, or MgO.[1] However, a bulk synthesis procedure for c-GaN has not been described. In contrast, the ordinary hexagonal form (h-GaN) and the nanocrystalline mixed-phase form (h/c-GaN) have multiple synthesis routes.[2,3] Ammonothermal methods have been used to obtain metastable or otherwise unobtainable nitride materials such as Mn_3N_2 at modest temperatures.[4] Crystals of h-GaN have been grown under ammonobasic conditions,[5] and h-AlN has been synthesized ammonothermally under both acidic and basic conditions.[6] Nanocrystalline GaN[7] and cubic BN[8] have also been prepared solvothermally. This communication describes the synthesis of bulk c-GaN by ammonothermal reactions of gallium metal and compounds under acidic (NH_4X; X = Cl, Br, I) conditions.

Anhydrous ammonia was condensed (at −196 °C) into a 7-in.-long, 5-mm o.d., 3-mm i.d. quartz tube containing the reactants and the tube was flame-sealed at a height (interior measure) of about 13−14 cm.[9] The exterior of the tube was pressurized with water inside a MRA-114R pressure vessel attached to a LECO HR-1B hydrothermal system to about 10 000 psi, and the pressure vessel was heated in a vertical orientation. All reaction temperatures were measured in the thermowell near the bottom of the pressure vessel (hot zone). The temperature gradients going up the tube were substantial, on the order of −10 °C/cm.[10] After completion of the temperature program, the tubes were allowed to cool at a natural rate (up to 2 h) to less than 200 °C before lowering the furnace, and to room temperature before removal from the pressure vessel. All tubes were frozen at −196 °C before opening, and the products were washed and air-dried.[11] A listing of experiments is provided in Tables 1−3, and Table 1 is organized into groups that reflect the parameter(s) that were varied. The fraction of each GaN product in the hexagonal and cubic phases was determined by comparison of its X-ray powder pattern to that of a well-ground 50:50 mixture of h-GaN and c-GaN.[12]

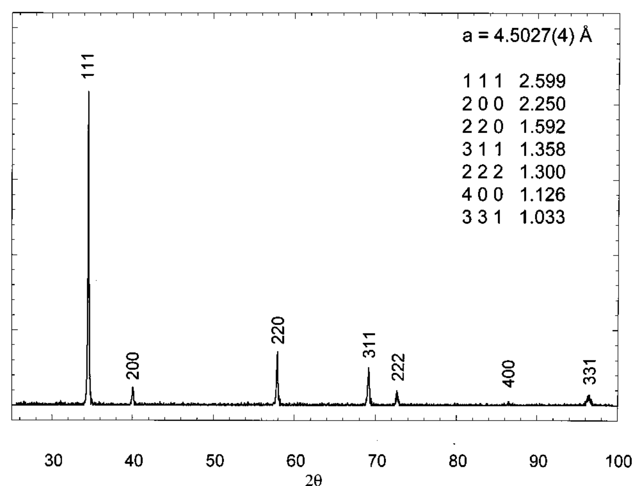
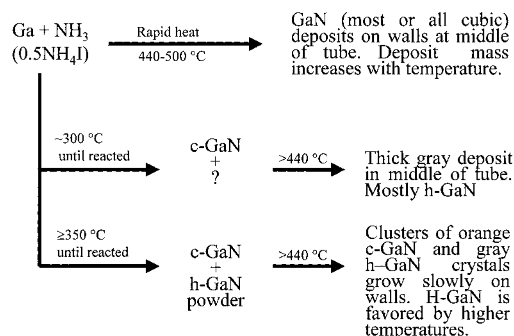


Figure 1. X-ray powder pattern (Cu Kα radiation) of c-GaN deposit obtained from exp 14.

Scheme 1. Effect of Temperature Program on Crystal Growth



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(9) All solid reactants were handled in a Vacuum Atmospheres Drilab. The anhydrous NH_3 (Air Products) was used as received. Gallium iodides were prepared in the melt by stirring stoichiometric amounts of Ga and sublimed I_2 under vacuum while heating to 240 °C over 1 h. GaI_3 and NH_4X were vacuum sublimed before use. *Proper eye and hand protection must be used when handling NH_3 filled tubes.*

(10) The relationship between the temperature inside a tube and the reading from the thermowell was determined by suspending a fine Zn (mp = 420 °C) wire from the top of a fine quartz fiber sealed inside a tube with NH_3 (58% fill) and measuring the height to which the wire melted after the tube was cooked. The temperature at any given height (cm) inside the tube fit the equation: actual temperature = reading − (24 + 10 × height) °C, valid for 450 ≤ reading ≤ 510.

(11) Washed with alcohol and acetone. Some samples were prewashed with aqueous hydrochloric acid to remove the precipitates formed from the exposure of NH_3 solutions of Ga halides to air. GaN is insoluble in aqueous HCl.

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Table 1. Experimental Data for Synthesis and Crystal Growth of GaN from Ga Metal and Ga Iodides[†]

exp	reactants (mg)	mmol NH_3	fill (%)[a]	temp pgm., °C[b] (16.67 h unless noted)	products: appearance, X-ray analysis, and yield: bottom of tube[c]	yld (mg)[d]	middle of tube[c]	yld (mg)[d]
(I) No Acid, or a Small Amount of NH_4I								
1	Ga (20)	19.2	58	495		no reaction		
2	Ga (33), NH_4I (2.5)	19.7	61	413	ow pdr, 95% h-GaN	24	nothing	
3	Ga (18), NH_4I (3.5)	20.1	59	506	gr pdr, 85%h-GaN	9	yl dep, 90% c-GaN	4
(II) ~0.5 molar equiv of NH_4I, Temperature Varied								
4	Ga (22), NH_4I (23)	–	66	204		no reaction		
	above tube			reheat 261	yl pdr + Ga metal			
	above tube			reheat 298	tan pdr, 95%c-GaN[e]	–	nothing	
5	Ga (27), NH_4I (26)	19.7	64	318	tan-wh pdr, 55% c-GaN +Ga metal		nothing	
6	Ga (26), NH_4I (26)	19.7	64	349	ow pdr, 65% h-GaN	22	nothing	
7	Ga (31), NH_4I (32)	19.2	60	383	ow pdr, 55% h-GaN	–	nothing	
8	Ga (31), NH_4I (30)	19.2	57	406	ow pdr, 50% h-GaN	–	nothing	
9	Ga (29), NH_4I (29)	19.2	62	425	ow pdr, 65% h-GaN	29	nothing	
10	Ga (31), NH_4I (31)	19.7	65	430	ow pdr, 75% h-GaN	19	nothing	
11	Ga (28), NH_4I (28)	19.2	63	446	ow pdr, 75% h-GaN	17	yl dep, 100% c-GaN	3
12	Ga (27), NH_4I (28)	19.2	64	448	ow pdr, 80% h-GaN	21	yl cls, 100% c-GaN	1.0
13	Ga (22), NH_4I (16)	–	61	470	nothing		or dep, 80% c-GaN	21
14	Ga (20), NH_4I (20)	19.2	60	497	nothing		or dep, 100% c-GaN	19
(III) 1 molar equiv of of NH_4I								
15	Ga (30), NH_4I (60)	19.7	64	453	ow pdr, 100% h-GaN	14	yl-or cls, 75% c-GaN	0.9
16	Ga(70), NH_4I (140)	–	64	514		gr cls, h-GaN[f]		
(IV) 0.5 molar equiv of NH_4I, Fill Varied								
17	Ga (25), NH_4I (25)	12.8	42	459	ow pdr 85% h-GaN	3	or dep, >95% c-GaN	6.5
18	Ga (28), NH_4I (28)	22.4	72	461	ow pdr, 100% h-GaN	13	or cls, c-GaN	0.1
(V) Multistep Temperature Programs								
19	Ga (42), NH_4I (38)	19.7	59	305 (48h); 25; 410	ow pdr, 80% h-GaN	31	nothing	
20	Ga (31), NH_4I (30)	19.2	59	306 (40h); 25; 455	–		gr dep, 95% h-GaN	21
21	Ga (19), NH_4I (18)	18.3	62	350; 455	ow pdr, 50% c-GaN	8	or cls, 100% c-GaN	5
22	Ga (37), NH_4I (39)	19.2	60	360; 510	nothing		yl+wh cls,85% h-GaN	40
23	Ga (28), NH_4I (28)	19.7	58	405; 455	ow pdr + or cls, 65% h-GaN[g]	10	or+gr cls, 95% c-GaN	10
(VI) NH_4Cl or NH_4Br Mineralizer								
24	Ga (25), NH_4Cl (9)	19.8	63	453	ow pdr, 100% h-GaN	>8	gn dep, 100% c-GaN	3.5
25	Ga (40), NH_4Cl (13)	13.0	41	454	ow pdr, 100% h-GaN	5	ow dep, 60% h-GaN	0.2
26	Ga (20), NH_4Br (20)	20.1	64	455	ow pdr, 65% h-GaN	3	yl+gr cls, 80% c-GaN	12
27	Ga (28), NH_4Br (19)	19.7	66	466	ow pdr, 60% h-GaN	2	yl+gr cls, 70% h-GaN	15
(VII) GaI_2 or GaI_3 Precursor								
28	GaI_2 (100)	19.4	~60	435 (64 h)	ow pdr, 80% h-GaN	4	ub- or dep 90% c-GaN	13
							lb- gr dep 60% h-GaN	15
29	GaI_2 (100)	19.5	62	350; 25; 455	ow pdr, 80% h-GaN	10	gr dep, 100% h-GaN	14
30	GaI_3 (80)	19.2	61	416	or pdr, 100% c-GaN	6	nothing	
31	GaI_3 (100)	19.2	64	419	or-tan pdr, 80%c-GaN	11	nothing	
32	GaI_3 (273)	19.2	–	466	gr pdr, 60% h-GaN	17	or dep, >95% c-GaN	6
33	GaI_3 (200)	20.1	66	491	nothing		or dep, 100% c-GaN	12

[†] Legend: pdr, powder; dep, deposit; cls, clusters of crystals; –, datum not available; or, orange; yl, yellow; gr, gray; gn, green; wh, white; ow, off-white; ub, upper band; lb, lower band. [a] Fraction of volume filled with solid and liquid at room temperature. [b] Actual temperatures measured in thermowell at least 3 h after heating begins (typically ~50 °C below furnace setting). The furnace on time at each temperature is 16.67 h unless noted otherwise. [c] Percentages are indicate the fraction of crystalline GaN in the cub and hex forms only. [d] Isolated yield. Not measured for all experiments. [e] May contain an amorphous product. [f] Tube burst from excess H_2 pressure when exterior counterpressure was relieved. [g] C–GaN clusters may have fallen from above.

Table 2. Synthesis and Analysis of Selected Gallium–Imide–Iodides

batch	synthesis[a]: GaI_3 (g)	KNH_2 (g)	silicone (mg)	KNH_2:GaI_3 ratio	yield (g)	elemental analysis (wt %): Ga	N	H	I	IR spectrum (KBr pellet)
a	3.50	1.29[b]	<10[d]	3.01	0.98	53.95	15.54	1.26	24.88	3203(s), 2970(m), 2200(w,br), 1510(m), 1091(vs),[f] 963(s), 795(m)
b	2.88	1.07[c]	none	3.04	0.61	64.25	21.21	1.97	8.39	3195(s), 2965(m), 2210(w,br), 1512(m), 966(s)
c	1.00	0.38[c]	17[d]	3.14	0.21	61.96	20.80	2.09	10.86	3217(s), 2960(s), 2220 (m,br), 1530(m), 1262 (m), 1091(vs),[f] 804(s), 545(s), 475(s)
d	2.00	0.68[c]	35[e]	2.80	0.62	59.82	15.65	1.71	10.27	3164(vs), 2964(s), 2170(m,br), 1510(m), 1303 (w), 1263(m), 1100 (sh),[f] 993(vs), 801 (m)

[a] In a 100-mL H-tube with a vacuum jacketed filter arm, KNH_2 was added to a solution of GaI_3 in anhydrous NH_3 containing silicone. The pressure in the attached vacuum line was regulated at 1 atm by a Hg bubbler which controlled the NH_3 temperature at −33 °C. The reaction was stirred for about 15 min and filtered. The white solid on the frit was washed 3 times with recondensed NH_3 and then the ammonia was vented and the product dried in vacuo. [b] Several years old, slightly yellowed. [c] Freshly prepared. [d] Dow Corning silicone grease (composition (from MSDS): 91% poly(dimethylsiloxane), 9% silica gel). [e] Poly(dimethylsiloxane). [f] Indicative of reaction with silicone grease or Si oil.

Gallium metal reacted slowly with supercritical NH_3 in the presence of at least a small amount of NH_4I, forming GaN as the only crystalline product at temperatures somewhat above 250 °C. At temperatures below ~440 °C, all of the GaN product remained at the bottom of the tube as a fine, off-white to tan powder. Although the products of a lower temperature (~300 °C) reaction (exp 4) showed mainly peaks for c-GaN (Figure 1) in its X-ray powder pattern, large peaks for h-GaN were present in the powder patterns of products that were either produced at (exp 2, 3, and 5–10) or reheated (exp 19 and 20) to higher temperatures. Thus, the lower temperature reactions seem to have produced both c-GaN and either a soluble or an amorphous product that could be thermally transformed to h-GaN.

(12) A 50:50 mix powder pattern (Cu Kα), 2θ (identity, I/I_0): 32.4 (h, 35), 34.5 (c + h, 100), 36.9 (h, 56), 40.0 (c, 21), 48.0 (h, 10), 57.9 (c + h, 30), 63.4 (h, 12).

Table 3. Experimental Data for Synthesis of GaN from Gallium−Imide−Iodides[†]

exp	reactants (mg)	fill (%)[a]	*T*, °C (16.67 h)[b]	products: appearance, X-ray analysis[c], and yield[d]	
				bottom of tube	middle of tube
34	Ga−NH−I a (20), NH_4I (20)	65	276	yl pdr, c-GaN shp, 9 mg	nothing
35	Ga−NH−I a (90), NH_4I (120)	65	500	or pdr, >98% c-GaN, 7 mg	or dep, >98% c-GaN, >20 mg[f]
36	Ga−NH−I b (50), NH_4I (50)	64	316	yl pdr, c-GaN, brd, 34 mg, 40 Å[e]	nothing
37	Ga−NH−I b (59), NH_4I (61)	64	372	yl pdr, c-GaN, brd, 37 mg, 50 Å[e]	nothing
38	Ga−NH−I b (50), NH_4I (50)	64	411	or pdr, c-GaN, brd, 29 mg, 90 Å[e]	nothing
39	Ga−NH−I c (31), NH_4I (44)	58	374	or-yl pdr c-GaN brd+shp, 15 mg	nothing
40	Ga−NH−I d (64), NH_4I (66)	65	280	yl pdr c-GaN shp, 10 mg	nothing
41	Ga−NH−I d (58), NH_4I (60)	64	375	or pdr, c-GaN, shp, 21 mg	nothing

[†]Legend: pdr, powder; dep, deposit; brd, broad diffraction peaks; shp, sharp diffraction peaks; or, orange; yl, yellow [a−d]See Table 1 footnotes for these items. [e]Crystallite size from Scherrer eqn. using 34.4 ° peak. [f]Anal. Found (calcd) for GaN: Ga, 82.88 (83.28); N, 16.39 (16.73).

At temperatures above ~440 °C, some or all of the product transported solvothermally, and polycrystalline material grew in the middle to upper portion of the tube (e.g., exp 11−14). The estimated temperatures in the growth zones were in the 350−410 °C range.[10] This result implied that the transport direction was from hot to cold, which was contrary to the cold to hot transfer observed for AlN.[6b] The microcrystals nucleated on the quartz surface and typically grew as wedges perpendicular to the surface or as clusters of needles or wedges growing from a point (Figure 2). When crystals of both the cubic and hexagonal forms grew, the cubic form had a tendency to predominate at the cooler end of the growth zone (exp 28 is a striking example). The composition and amount of deposited material was highly dependent on the temperature program (Scheme 1). High deposition rates were also favored by low fill factors, at least with NH_4I mineralizer (exp 17 and 18). Some of the irreproducibility in the results may be explained by uncontrolled variables such as the condition of the quartz surface,[13] random mechanical transport of seeds, or variations in the thermal gradient from the hydrothermal transport of quartz onto the pressure vessel walls and the tube exterior. However, the basic trends were fully reproducible.

Cubic GaN was prepared with a NH_4Cl or NH_4Br mineralizer instead of iodide (exp 24−27). Although bromide afforded the fastest crystal growth rates, it also resulted in substantial amounts of large h-GaN needles. The halide ion determined the color of the c-GaN crystals: I^-, orange to yellow; Br^-, yellow; Cl^-, green. The h-GaN crystals were always gray to white.[14]

Both cubic and hexagonal GaN deposits were grown using GaI_2 or GaI_3 (exp 28−33).[15] The triiodide reacted with NH_3 above 400 °C to form mostly c-GaN, while GaI_2 disproportionated to Ga and GaI_3 immediately upon dissolving in NH_3. Gallium diiodide[16] was an

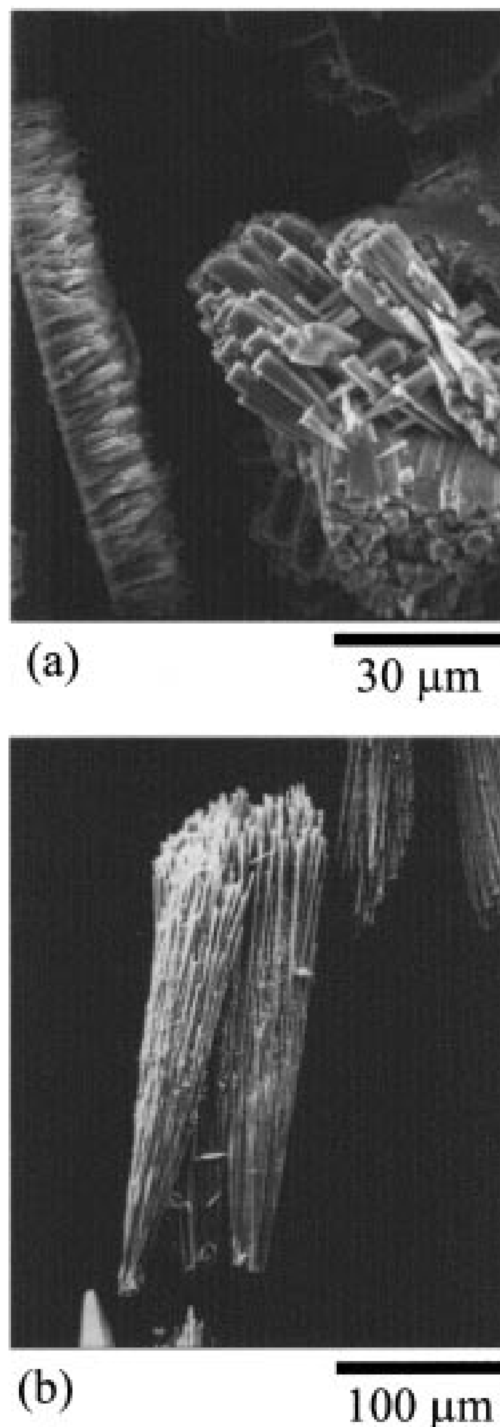

Figure 2. Scanning electron micrographs (25 KV) of (a) c-GaN and (b) h-GaN crystals from exp 14 and 16, respectively.

(13) The condition of a quartz surface was found to greatly affect the growth of BP which has identical lattice parameters to c-GaN: Chu, T. L.; Jackson, J. M.; Smeltzer, R. K. *J. Cryst. Growth* **1972**, *15*, 254.

(14) Only a very weak visible photoluminescence (usually orange) was observed from any of the well-crystallized c-GaN samples on long-wave UV irradiation, but the emission of most nanocrystalline samples was noticeably stronger (particularly if washed[3c] with hydrochloric acid), and the Ga−NH−I samples a, b, and c photoluminesced with an intense white to yellow light. The photoluminescence from the nanocrystalline c-GaN from exp 36 was only a dull yellow when first prepared, but was a bright orange after several days air exposure, and became an extremely intense yellow after a wash with dilute HCl.

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efficient precursor for the growth of phase-pure deposits of hexagonal GaN (exp 29).

A gallium imide−iodide material was prepared from GaI_3 and KNH_2 in liquid NH_3, and was identified as an imide from elemental analysis and a comparison of its IR spectra to $Ga(NH)_{1.5}$[3b] (Table 2). The results of ammonolysis experiments with gallium imides had a lot of variation that was dependent on which batch Ga−NH−I was used in a particular experiment (Table 3). Some batches (a and d) produced c-GaN with a sharp X-ray powder pattern readily upon ammonolysis with NH_4I at temperatures as low as 275 °C. Other batches (b) only produced nanocrystalline c-GaN at temperatures as high as 411 °C. One critical requirement for low-temperature c-GaN production appeared to be the presence of a small amount (<1 wt %) of Si grease or poly(dimethylsiloxane) in the imide synthesis reaction (compare exp 34, 40, and 41 to exp 36−38). Avoiding the use of excess KNH_2 in the imide synthesis also seemed to be helpful for obtaining well-crystallized c-GaN (compare exp 39 to 41). However, the imide compositions were often difficult to reproduce, and there is much that remains to be understood about this method.

In conclusion, the ammonothermal synthesis of c-GaN appears to be a complicated, kinetically controlled process. Although h-GaN was thermodynamically favored, crystals of c- GaN were formed through an unknown process with a low activation barrier, and these crystals probably acted as seeds for the growth of bulk c-GaN. By using seed crystals and carefully controlled conditions, it may be possible to obtain c-GaN crystals of sufficient size and quality to be used as native substrates for device manufacture. However, it is likely that substantial additional study of the growth and transport chemistry will be necessary to determine exactly what conditions and apparatus are required.

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