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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Ammonothermal synthesis of thick gallium nitride film employing acidic mineralizers

**Dirk Ehrentraut · Yuji Kagamitani · Akira Yoshikawa ·
Naruhiro Hoshino · Hirohisa Itoh · Shinichiro Kawabata ·
Katsushi Fujii · Takafumi Yao · Tsuguo Fukuda**

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Abstract Fabrication of wurtzite-type gallium nitride (GaN) thick films on HPVE-grown {0001} GaN substrates under moderate ammonothermal conditions is reported. Supercritical ammonia (NH_3) as solvent and the mineralizer ammonium chloride (NH_4Cl) is employed for temperature and pressure conditions of 400–550 °C and ≤135 MPa, respectively. Growth rates of 30 μm per day over long-term growth runs were obtained. The effect of surface morphology of the substrate on homoepitaxial nucleation of GaN films prepared from ammonoacid solutions is investigated. Two-dimensional nucleation is obtained for substrates etched by hot concentrated KOH prior film growth. In this case the interface between film and the $(000\overline{1})$ substrate does not show any signs of voids or island nucleation. Cracking pattern reveals similar mechanical-elastical properties for film and substrate.

Introduction

The device technology for the wide band gap semiconductor gallium nitride (GaN, $E_g = 3.42$ eV at 300 K [1]) is much advanced over the growth of free-standing single-crystalline bulk material, which is in strong contrast to former developments in classical semiconductors like silicon or gallium arsenide. In fact, lacking of thermal and lattice-matched GaN substrates impedes the cost-effective fabrication of low-defect (low-loss) devices, which would bring a new quality in terms of energy-efficiency and lifetime. Particularly, white solid-state-light sources realized by GaN high-brightness light emitter diodes (LED) are expected to soon make a major contribution to the large market for general illumination. Despite strongly reduced size and long-term durability of the device, the energy-saving (up to 90% by contrast to conventional candescent bulb lamp) and environmental aspects are clearly an advantage of the GaN technology. GaN LED technology is free from arsenic and mercury.

Due to thermodynamic limitation, GaN can be grown from the stoichiometric melt solely at extreme pressure and temperature of >6 GPa at 2,220 °C [2]. On the other hand, high-pressure (≥100 MPa) solvothermal techniques are well established and currently growing the largest α-SiO_2 [3] and ZnO [4] crystals from supercritical (SC) aqueous solutions.

Solvothermal techniques do comprise a class of technologies capable to fabricate nano to macro-size, quasi-amorphous to single-crystalline solid state matter. Basic principle is the use of a liquid polar solvent (ammonia, NH_3, in case of GaN), which forms metastable intermediate products with the solute (nutrient, mainly GaN and metallic Ga for GaN growth). Mineralizers are essential to amplify the process of nutrient dissolution and deposition. If a closed system is utilized, due to developing high system pressure often the solvent transforms into its supercritical state (for NH_3 $T_c = 132$ °C, $p_c = 11.2$ MPa). This further fosters solubility of the nutrient.

D. Ehrentraut (✉) · Y. Kagamitani · A. Yoshikawa ·
N. Hoshino · T. Fukuda
Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577,
Japan
e-mail: dirk@tagen.tohoku.ac.jp

H. Itoh · S. Kawabata
Mitsubishi Chemical Corp., 1000 Higashi-Mamiana, Ushiku,
Ibaraki 300-1295, Japan

K. Fujii · T. Yao
Center for Interdisciplinary Research, Tohoku University,
6-3 Aramaki Aza Aoba, Aoba-ku, Sendai 980-8578, Japan

Merits of the solvothermal crystal growth technology comprise: (a) operation near the thermodynamic equilibrium with ability to generate a high crystallinity due to zero temperature gradient at the interface of growing crystal with surrounding solution; (b) large crystal quantities can be controlled over long processing time enabling a high throughput; (c) environmentally benign conditions for production; (d) over 60 years in use for diverse mass-produced crystals, such like quartz [5].

The great potential of solvothermal techniques for crystal growth on an industrial scale is demonstrated by the story of industrial growth of α-SiO_2 (low temperature phase of quartz), which dates back to the 1940s. In 1953, Walker [5] published the hydrothermal synthesis of quartz crystals over periods less than two months and weighing over 1 lb (453.6 metric grams). Autoclaves sizing 10 cm internal diameter (I.D.) and 122 cm internal length (I.L.), the temperature difference method and quartz nutrient was employed. Walker already pointed out that crystals grown from solutions are likely of more perfect quality than those grown from melts.

In the hydrothermal growth of ZnO, already about 100 crystals of 2 inch size can now be grown per cycle [4]. ZnO in fact is the first semiconducting crystal, which is grown on an industrial scale by a solvothermal route.

The ammonothermal growth of GaN is the youngest among the solvothermal techniques aiming to yield large single crystals and still is at research level. Very recently, the successful ammonothermal growth of a 1 inch size (0001) GaN crystal has illustrated the potential of the ammonothermal technique [6]. Applied temperature and pressure was 625–675 °C and about 214 MPa, respectively. Another recent paper [7] has demonstrated single crystals of $\leq 10 \times 10 \times 1\ \text{mm}^3$ in size grown under the conditions of 475–625 °C and 100–300 MPa. A growth rate up to $50\ \mu\text{m}\ \text{d}^{-1}$ was achieved. Both papers employed the basic mineralizers $NaNH_2$ + NaI and KNH_2, respectively.

The use of basic mineralizers causes the retrograde solubility of GaN [7, 8], i.e., a lightly increased temperature in the growth zone over the zone for dissolving the feedstock is required to initiate nucleation. By contrast, growth from acidic mineralizers employs reduced temperature and pressure and provides a regular solubility, which is a considerable advantage to the technology in that it allows to terminate the GaN growth by avoiding an undersaturated state of the solution [9]. More clearly, slow cooling can be applied only in the case of growth from acidic mineralizers.

Beneficial is the fact that acidic mineralizers are easy to handle due to sufficient chemical stability. In the series of NH_4X (X = Cl, Br, and I), the melting point raise from 340 to 551 °C [10] due to increasing bonding strength.

We report here on our recent efforts in the ammonothermal growth of wurtzite-type GaN from the NH_4Cl at relatively low temperature (≤550 °C) and pressure (≤150 MPa). Particularly, as nucleation on the substrate is of paramount importance for the quality of a growing crystal we aimed to find suitable conditions for fabrication of single crystalline films. The effect of feedstock and surface morphology of the substrate is analyzed in the light of growth rate and crystallinity of the grown film.

Experimental conditions

Details on experimental conditions were already given in Refs. [9] and [11]. We work with Pt-lined autoclaves (30–60 mL) to prevent from possible contamination from the stainless steel of the autoclave. The Pt inner liner was separated by a Pt baffle into bottom zone (high temperature to dissolve the nutrient) and upper zone (lower temperature for crystal growth). The nutrient consist of Ga metal (99.9999%) and polycrystalline GaN (better 99.99%) in different ratios and NH_4Cl (99.999%) is the mineralizer. Both were placed in the high temperature zone. Self-standing [0001] GaN single crystals grown by HVPE were prepared for substrates. Except for one experiment, the $(000\bar{1})$ face (N-terminated) and the (0001) face (Ga-terminated) were both well polished, i.e., scratch-free. Seeds were cut into $10\ \text{mm}^2$ squares and afterwards mounted in the low temperature zone. GaN growth was performed at temperatures ≤550 °C under pressures of ≤150 MPa. Filling of the autoclave was 65%. The growth temperature was kept constant for either 96 or 240 h. The ratios of the molar concentration $c_{\text{m/p}}$ of mineralizer NH_4Cl and precursor was kept at $0.10 < c_{\text{m/p}} < 0.13$. In typical experiments the weight of the reactants for the 30 ml autoclave would be like 0.4–1.8 g Ga, 8–9 g GaN, 0.7–0.75 g NH_4Cl and 0.69–0.73 mol NH_3.

Differential interference microscopy (DIM) and scanning electron microscopy (SEM; JEOL, JSM-7000F) to monitor surface morphologies and energy dispersive spectroscopy (EDS; SEM JEOL, JSM-7000F, 15 kV, 1 nA, accumulation time around 60s) to analyze the chemical nature was used. X-ray reciprocal space mapping (XRSM) and X-ray rocking curve (XRC: Rigaku, ATX-G) measurement was performed to study crystallinity and orientation of the film. The diffractometer with CuK_α radiation was employed in combination with a four crystal Ge(220) channel monochromator, beam divergence 12 arcsec, scan speed $0.01°\ \text{min}^{-1}$, and step width 10^{-4}.

Results and discussion

Figure 1 presents an over 200 µm thick, virtually colorless GaN crystal grown at 550 °C and ≤150 MPa from an autoclave of 16 mm I.D. The substrate was HVPE-grown GaN with an as-grown surface, i.e., no machining was applied. Cracking was not observed since the HVPE substrate was crack-free with low residual strain as observed by optical microscopy. The yellowish coloration is due to some crystallization on top of the grown film while the system cooled down to room temperature, and can be removed relatively easy by water and 2-propanol. The average growth rate was about 20 µm d^{-1} for the growth duration of 10 days. A higher growth rate of almost 30 µm d^{-1} was already reported by our group along with tuning the growth rate by modifying the precursor [9]. A mixed Ga/GaN precursor yielded abovementioned growth rate. For long-term experiments we would prefer purely GaN as precursor whereas short-term experiments of a few days will require a significant amount of Ga. This is due to the fact that the Ga reacts quickly with the mineralizer containing ammonia and the reaction dynamics is much more slowly in case of GaN. Later effect is important to provide feeding over long growth time.

Fig. 1 Image of a 0.2 mm thick ammonothermal GaN crystal grown on $(000\bar{1})$HVPE GaN substrate

The crystallinity of the sample in Fig. 1 was investigated by XRSM. Figure 2 reflects the *ω*/*ω-2θ* maps for the Ga-terminated and N-terminated faces, respectively. The (0004) reflection was employed, which refers to a penetration depth of 18 µm for CuK*α* radiation. There is a double peak observed for the (0001) face, which can be understood in terms of superposing peaks from substrate and film. This effect was recently interpreted in such way [9] and gets clearer by knowing that the film thickness on the (0001) face is typically thinner than on $(000\bar{1})$.

X-ray rocking curve measurements revealed the full-width half-maximum (FWHM) from (0004) reflection for *ω* and *ω-2θ* for the Ga (N)-terminated face of 610 (480) and 310 (330) arcsec, respectively. This value shows an improvement to our recently published results of 610–2160 arcsec [9] and can be attributed to the higher substrate quality in combination with improved nucleation control. The FWHM of XRC *ω-2θ* scans employing (0002) reflection is 220 and 300 arcsec for the (0001) and $(000\bar{1})$face, respectively. These values are clearly better than for recently reported ones for about 0.4 mm thick crystalline GaN films grown from basic mineralizer [7].

Using NH_4Cl and a 1-inch large HVPE seed yielded an about 0.4 mm thick single-crystalline GaN film at a growth temperature of about 500 °C and <130 MPa system pressure (Fig. 3). The crystal appears in a translucent brownish coloration due to defects [12]. Also, nitrogen deficiency has been claimed to cause a dark coloration [7]. Cracks from the seed crystal continued into the grown crystal. Nevertheless, the feasibility to produce large GaN crystals from acidic ammonothermal conditions under significantly lower pressures and temperatures than from basic mineralizers is clearly evidenced. The average growth rate was lightly less than 30 µm d^{-1}.

The film in Fig. 3 shows a tendency for columnar growth, which is the result of island nucleation and growth. Insufficient conditions of the substrate surface, i.e., damage due to machining is claimed to cause this effect. In an attempt to further evidence the effect of surface quality of

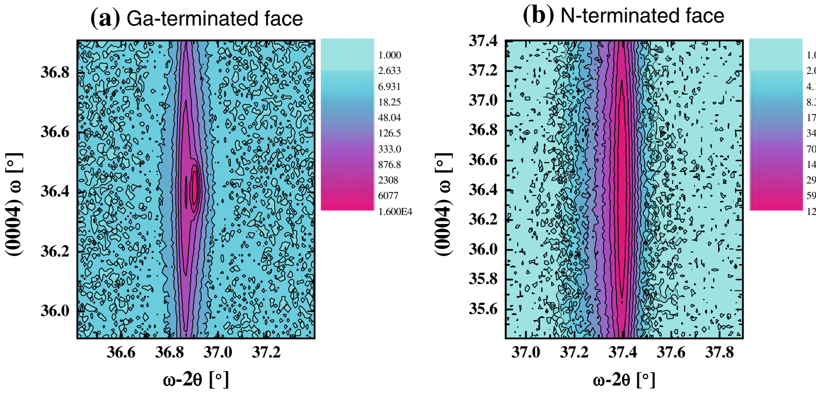

Fig. 2 X-ray space maps from specimen in Fig. 2. The (0004) reflection was used. Intensity is color coded

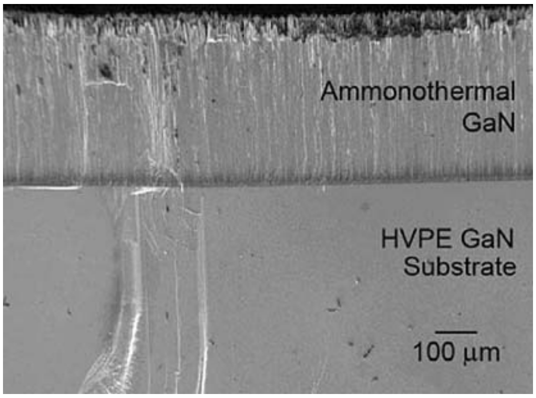

Fig. 3 Cross-sectional SEM image of the 0.4 mm thick ammonothermal GaN crystal grown on $(000\bar{1})$ HVPE GaN. Image is contrast-enhanced

the HVPE-GaN substrate on nucleation and growth behavior of the acidic ammonothermal GaN film, we applied a simple etching procedure making use of concentrated KOH as the etchant. However, KOH etching is only effective on the N-terminated face and was explained to originate from bonding configuration of N at the surface, particularly the dangling bond of the N should play an important role in this selective etching of the polar GaN surfaces [13].

Figure 4 shows comparing cross-sectional SEM images from a GaN film nucleated on a $(000\bar{1})$ HVPE-grown GaN substrate, mechanically polished and successively etched with KOH (Fig. 4a) and solely mechanically polished (Fig. 4b) prior growth. Both substrates contained low residual strain, quite similar to the one in Fig. 1. The film thicknesses are around 1 and 10 µm, respectively. The surface does appear similar with the already reported cobble pattern, suggesting similar growth modes for the both films [9]. The interface between substrate and film in Fig. 4a appears straight and any signs of dissolution as well as voids have not been found. We suggest that the mechanical properties and consequently the crystallinity are much higher for the film grown on the etched crystal face as the similarity of the cracking pattern from seed and film is quite striking. We further suggest that the film in Fig. 4a followed a 2 dimensional (2-D) growth mechanism rather than island-nucleation-and-spread mechanism. A respective magnified and contrast-enhanced image from the interfacial region is shown on top of Figs. 4a and b, respectively.

The GaN film nucleated on the solely polished substrate in Fig. 4b clearly reveals a different cracking pattern than for the substrate. Small voids were sometimes observed at the interface.

A more general observation is that apparently the crystal quality is slightly higher for GaN nucleated on the $(000\bar{1})$ face than for GaN nucleated on the (0001) face. This is coherent to the growth from basic mineralizers [6], although the reason for this variation is under speculation by now. This observation is quite in contrast to the growth of hydrothermal ZnO. On first sight, we conclude that the main growth species must be positively charged like the cationic octahedra $\left[\mathrm{Ga}(\mathrm{NH}_3)_5\mathrm{Cl}\right]^{2+}$ as proposed very recently [14]. This molecule is expected an effective precursor for the preparation of GaN. Above approach is pretty similar to the hydrothermal ZnO system, where growth species like $\mathrm{Zn}(\mathrm{OH})_4^{2-}$ are negatively charged and therefore preferably accumulate on the (0001) face of the ZnO seed crystal.

A striking difference to hydrothermal ZnO is that the growth rates in $\langle 0001\rangle$ and $\langle 000\bar{1}\rangle$ do not differ essentially according to the results in our small size equipment.

The surface morphology of the film in Fig. 4a is shown in Fig. 5. In this SEM image it is almost impossible to recognize any features except some surface contamination. This suggests a very flat surface, which is obviously due to

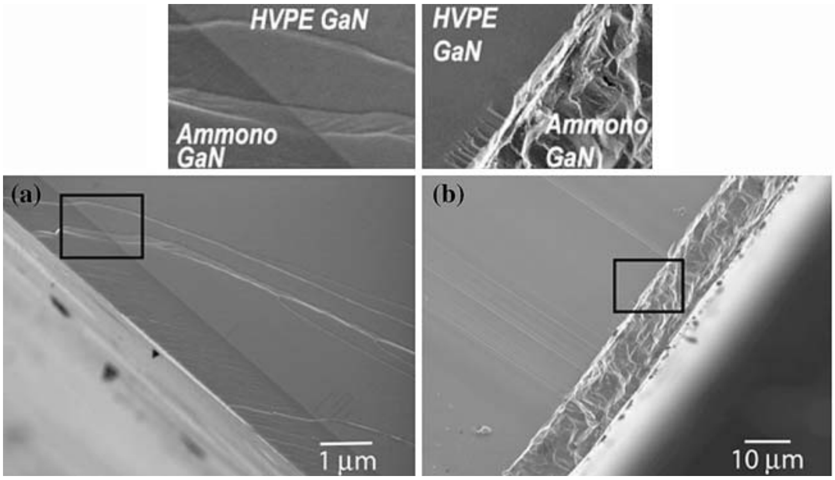

Fig. 4 Cross-sectional SEM images from a GaN film nucleated on a mechanically polished and successively etched (**a**) and solely mechanically polished (**b**) $(000\bar{1})$ HVPE-grown GaN substrate. The cracking pattern from seed into film is similar only for case (**a**). A magnified and contrast-enhanced image from the interfacial region is shown on top of (**a**) and (**b**)

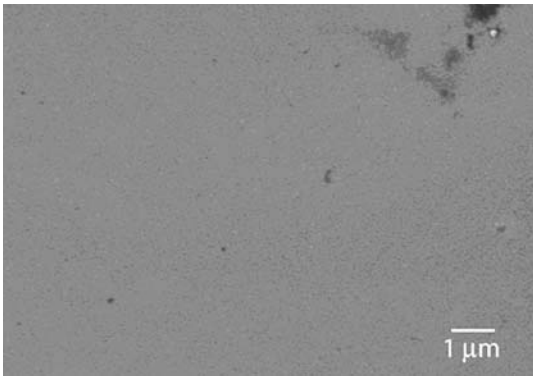

Fig. 5 SEM image showing the view down (000$\bar{1}$) plane of the film nucleated on the etched seed crystal (Fig. 4a). The surface is extremely flat with features about 100 nm in size

improved conditions for nucleation on the quasi damage-free surface due to etching.

Analysis of the composition of a high-quality GaN film of 20 µm in thickness by EDS measurement is shown in Fig. 6b, and is compared to that of the HVPE substrate in Fig. 6a. Fitting coefficient was 0.2573. Within the range of measurement of 0–10 keV, characteristic $K\alpha$ (9.241 keV) and $L\alpha$ (1.098 keV) lines due to Ga and of N are observed. The mineralizer would contribute chlorine as Cl$K\alpha$ line at 2.621 keV. A very weak oxygen contamination from all participating reactants and autoclave inner wall can be found at 0.525 keV ($K\alpha$). The chemical composition of the film (HVPE substrate, fitting coefficient 0.2964) was: 37.31 (40.08) at% Ga, 60.11 (57.20) at% N, 1.57 (2.06) at% O, 0.76 (0.41) at% Cl, and 0.25 (0.25) at% Br. The latter is below detection limit for both cases. The error was less than 1% except for Ga, which was 5.6 and 11.3 % for the film and substrate, respectively. Since the chemical composition of the ammonothermal GaN film and the HVPE-grown substrate as determined by EDS is similar within error range we conclude that single-phase GaN was grown.

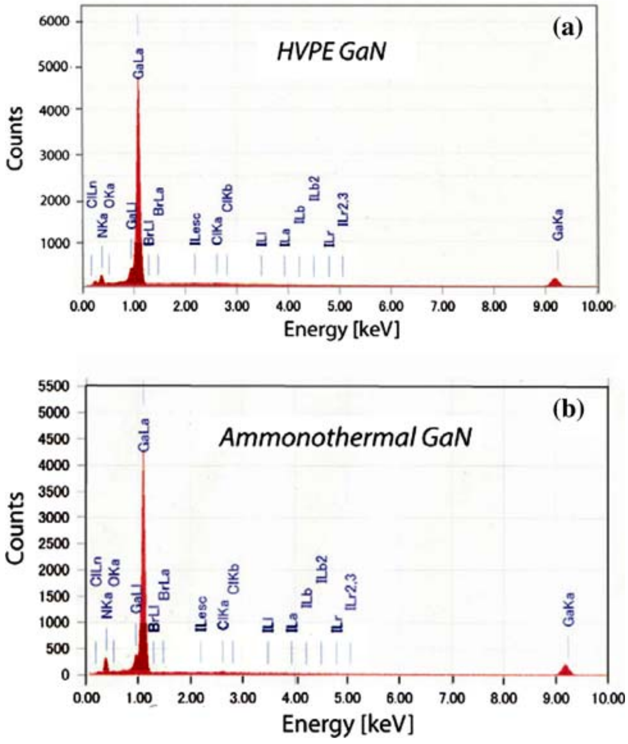

Fig. 6 Chemical analysis by EDS of an ammonothermal GaN film (**b**) in comparison to the HVPE substrate (**a**)

One might think that the presently low growth speed of 25–50 µm d^{-1} [7, 9] should impede from the application of ammonothermal growth technique to produce GaN in an economic fashion. On the other hand, the growth rate in the remarkable work on quartz by Spezia in the early 1900s [15] was estimated to maximum 20 µm d^{-1} [3]. Understanding the acting and interplay of the growth parameters along with better knowledge of the chemistry in the hydrothermal solution, surely a key role in ammonothermal GaN as well, has finally pushed the growth technology of quartz. Now, 500–600 µm d^{-1} growth rates are achieved in quartz production [16].

Finally, well-shaped and self-nucleated (0001) GaN crystals of >2 mm in length along c-axis and ≤0.1 mm diameter across have been grown at remarkably high growth rates up to almost 500 µm d^{-1} in best cases [17]. This is demonstrating the high potential of the ammonothermal technique with acidic mineralizers for large-scale production of bulk GaN. However, much work has yet to be done in the ammonothermal growth of GaN. Particularly the control of the mass transport is a key figure to improve the growth rate in the ammonothermal Growth of GaN.

Conclusion

Thick films of GaN have been fabricated from acidic ammonothermal conditions. The effect of substrate conditions on the nucleation of the films has been investigated. The structural quality of the substrate, particularly the appearance of a damaged surface layer due to machining, strongly determines the growth mode. Crack-free HVPE GaN substrates etched prior growth provides good conditions for 2-D nucleation. Films grown on the N-terminated face show a higher growth rate of presently 30 µm d^{-1} for long-term experiments.

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