Chapter 11
A Brief Review on the Na-Flux Method Toward Growth of Large-Size GaN Crystal

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Abstract The growth of bulk GaN by the Na-flux method is reviewed. The largest GaN crystal thus far produced is two inches in size with thickness of a few millimeters along (0001) axis. The historical development of the method, experimental conditions, and quality of the grown GaN crystals are summarized.

11.1 Introduction

The sodium (Na)-flux method in its original version is one of the older approaches to grow GaN; however, a relatively new development among all the techniques toward the crystal growth of bulk GaN is the Na-flux method as a liquid phase epitaxy (LPE) variant. Firstly, Na was named as the flux component, the other part being gallium (Ga), and later a larger number of other group-I and -II elements like lithium (Li), potassium (K), calcium (Ca), strontium (Sr), barium (Ba) have been worked with and their effects on the crystal formation was studied by various research groups in the past.

Major progress in terms of crystal size, quality, and scalability of the crystal growth system has been reported by the group from the Osaka University who employs the LPE technique [1]. The first growth of a 2-inch size GaN crystal has been reported in 2006 [2]. This chapter will therefore have its main focus on the achievements reported by the Osaka group, which by now is considered the leader in this particular technology, and will begin with a brief overview over the historical developments in the Na-flux technique.

11.2 Historical Development in Brief

Yamane et al. have observed in the mid-1990s that the synthesis of ternary nitrides like Ba_2ZnN_2, Sr_2ZnN_2, etc. from a Na flux sometimes yielded hexagonal GaN crystals as stable phase [3]. They consequently focused on the preparation of GaN

crystals from the Na flux using sodium azide (Na_3N) as Na source and were first to
report the growth of hexagonal GaN crystals up to 2 mm in size in 1997 [4]. Sealed
steel tubes were used at temperatures (T) ranging between 600 and 800 °C, pressure
(p) $\leq$ 11 MPa, and under nitrogen (N) excess. A high Na content is required to
form GaN and it was reported that the formation of GaN requires less amount of Na
when the temperatures rises. Moreover, the GaN size increased with decreasing Na
content in the Ga–Na solution.

This technology had been improved and soon Aoki and Yamane reported the
growth of up to 3 mm large GaN crystals with an X-ray full-width half-maximum
(FWHM) from the (0004) diffraction peak as small as 25 arcsec, synthesized by
heating a Na–Ga melt placed in a boron nitride (BN) crucible at $T = 750$ °C and
$p = 5$ MPa of N_2 for 200 h growth time [5]. Yields and morphology of GaN sin-
gle crystals varied with the molar ratio Na/(Na + Ga) in the starting composition.
Electrical properties were measured: resistivity of 0.04 Ωcm, carrier concentration
of 1–2×10^{18} cm^{-3} (n-type), and carrier mobility of 100 cm^2 V^{-1} s^{-1}. Cathodo-
luminescence (CL) spectra at room temperature revealed a single peak around
$\lambda = 362$–365 nm.

The crystal size was further increased to 3×5 mm^2 platelets and bulky pris-
matic crystals of 1 mm along the c-axis [6]. The average growth rates were 14 and
2 μm h^{-1} along c direction for the platelet and prismatic crystals, respectively.

Sodium was later speculated to act as catalyst for the dissociation of N_2 molecule
into N ions by donating electrons [7]. Consequently, a high content of Na would
accelerate the introduction of N ions into the Na–Ga melt where Na_x–(GaN_y) com-
plexes would be formed. This phenomenon has been further investigated by Iwa-
hashi et al. and Kawamura et al. [8, 12]. They concluded that N_2 would be ionized at
the gas–liquid interface of the Na flux at $T > 900$ K and successively entered into
the Ga–Na flux. Pressure is also promoting the solubility of N radicals. The addi-
tives Ca and Li in the Ga–Na flux improve the quantity of dissolved N, obviously
by the formation of a metastable phase in the flux, thus decreasing the N activity.

Some of the larger crystals are shown in Fig. 11.1. A maximum size obtained
for self-nucleated GaN crystals was around 6 mm along the c-axis. Using a self-
nucleated GaN crystal as seed, a second generation of GaN was deposited at $T =$
760 °C at low average growth rates around 0.2 μm h^{-1} for the nonpolar faces [9].
Li_3N was added to the flux to improve the solubility of N. Figure 11.2 compares the
size of a seed and a GaN crystal grown on such seed.

The growth rate for seeded growth was increased to about 2 μm h^{-1} though they
are assumed to be higher because of initial dissolution of the seed crystal [10].
Growth temperature and pressure were $T = 900$ °C and $0.8 \leq p \leq 7$ MPa of N_2
for 72 h and the Ga melt was heated in Na vapor, which forms the Na–Ga melt.

The presently largest GaN crystal grown by the Na-flux method was produced by
a group from the Osaka University [2, 12]. Figure 11.3 depicts the 2-inch size GaN
crystal fabricated on a (0001) HVPE-GaN substrate.

The first report by the Osaka group was published in 1998 [13]. In order to
increase the crystal size as well as obtaining oriented crystals, the LPE technique
employing a substrate was used successfully [14].
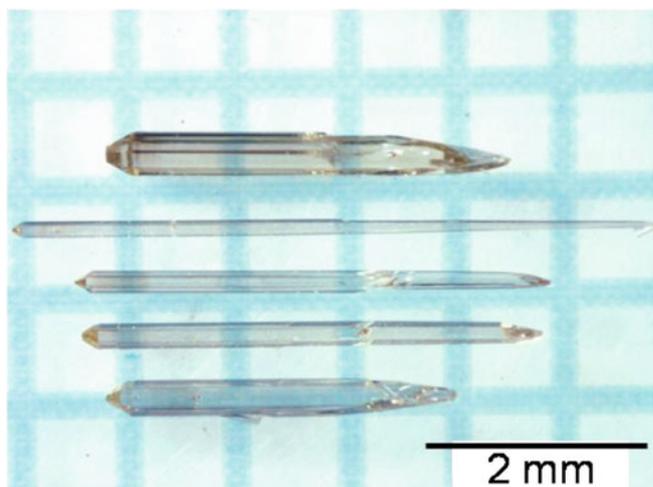
Fig. 11.1 GaN prismatic and needle crystals prepared at $900\,^\circ$C and 9.5 MPa for 400 h. (Image courtesy of H. Yamane, Tohoku University, Japan.)
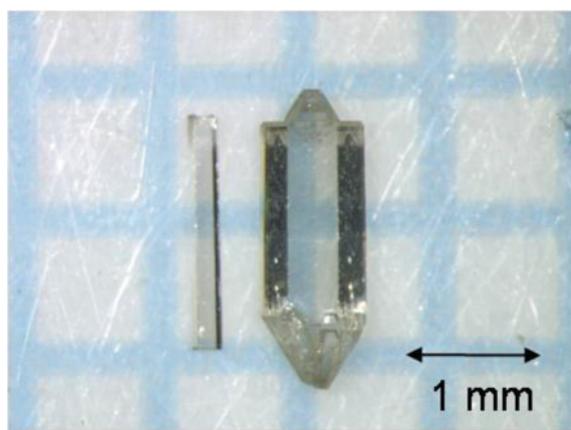
Fig. 11.2 Self-nucleated GaN seed and GaN crystal grown on the seed. (Image courtesy of H. Yamane, Tohoku University, Japan.)

It was recognized that a forced flow of the solution in the vicinity of the growing GaN crystal would lead to improve growth conditions, hence, leading to increase the growth rate. The flux-film-coated LPE method (FFC-LPE) was introduced in 2003 [15]. The heated growth chamber with the flux-containing crucible was mounted such that swinging could be applied. At a swing frequency of 1.5 min^{-1}, the growth rate of $4\,\mu$m h^{-1} at $T = 800\,^\circ$C was achieved although the nitrogen pressure was as low as $p = 0.95$ MPa.

Nonpolar substrates are also in the focus and the fabrication of an a-plane GaN substrate has recently been reported [16]. Strontium (Sr) was added as the additive to

Fig. 11.3 A 2-inch GaN crystal grown by the Na-flux LPE method. About 0.5 at% C had been used as additive to reduce the parasitic nucleation of GaN [12] (Reprinted with permission. © 2008, Elsevier Publishers.)

gain the desired morphology. X-ray diffraction revealed the improved crystallinity, i.e., the FWHM from the $(11\bar{2}0)$ reflection plane decreased from 1,152 to 236 arcsec for the GaN template (MOCVD GaN film on Al_2O_3) and the LPE-grown crystal, respectively.

Aside from the Na flux, there are some more attempts using alkaline and earth alkaline salts to obtain a reasonable solubility of GaN under moderate conditions. Feigelson and Henry have recently employed the system $LiF-BaF_2-Li_3N$ to grow GaN single crystals about 0.5 mm long [17]. The growth temperature was 800 °C and pressure about 2.5 MPa.

Song et al. used the mixture $Li_3N + Ga$ [18] and Wang et al. made use of the mixture $Li_3N + Ca + Ga$ [19] at temperature around 800 °C and around 200 kPa N_2 pressure. Free-standing GaN platelets of up to 4 mm in size were produced.

As appealing as all the above mentioned low temperature and pressure approaches are, it must be however noted here that apart from the technology currently under development at the Osaka University, bulk GaN crystals of sufficient size by the Na-flux or related flux methods are yet to be demonstrated.

11.3 Experimental Conditions for the LPE Growth of GaN by the Na-Flux Method

Experimental conditions are typically subject to modification in order to target a specific goal like doping, control of morphology, and the likes. Basically, the following procedure is employed according to [20]: Starting materials are Ga and Na,

both placed in an alumina crucible. A GaN/Al_2O_3 template would serve as seeding substrate and is placed at the bottom of the crucible prior to filling with the starting materials. A stainless steel tube resistant to high temperature and pressure is housing the crucible. Before mentioned steps are carried out in a glove box under argon (Ar) atmosphere to prevent the Na from the reaction with moisture from the air. Next, the steel tube is pressurized with N_2 gas and heated in an electric furnace. GaN crystals are typically grown in the Ga–Na solution by maintaining the temperature (around 850 °C) and pressure (around 5 MPa) over the entire growth time. After the growth has been completed, the tube is taken out from the furnace to remove the crucible, and the Na is dissolved in cold ethanol and water. Careful handling is requisite to prevent from strong reaction of the Na. Remaining Ga can be removed with ethanol and hot concentrated chloride acid.

11.4 Growth Mechanism and Dislocations

### 11.4.1 Effect of Flux Composition on Growth Stability and Crystal Morphology

The effect of additives on solubility, growth stability, crystal morphology as well as alloying with GaN was studied to improve the GaN crystal growth and eventually to prepare new phases.

Lithium increases the solubility of GaN probably through increased solubility of N [21]. Lithium-based fluxes like the Li_3N + Ga [18] and also Li_3N + Ca + Ga [19] were applied; however, it has been noted that excessive Ca in the flux hinders the formation of GaN. Bao et al. have recently reported the use of a flux composed of Ba_3N_2 + Ga to grow small crystals of GaN [22]. As for the flux with Ca, higher concentration of Ba strongly reduces the formation of GaN and also affects the growth rates of the different crystal facets; consequently, the morphology of the crystal can be modified.

Sekiguchi et al. have reported that using K instead of Na would yield cubic GaN crystals [23]. According to CL measurements, the cubic GaN crystals prepared and peaking around 3.2 eV were highly defective.

Iwahashi et al. illustrated the change of the crystal morphology that is caused by Sr as an additive to the melt [16]: As the portion of Sr was increased from 0 to 1.5 mol% with respect to Na, the formation of m-faces $\{1\bar{1}00\}$ gained strength at the cost of the pyramidal facets $\{10\bar{1}1\}$, Fig. 11.4. At 1.5 mol% Sr in the Na flux, self-nucleated GaN crystals would only be bound by both basal faces (0001) and $(000\bar{1})$, and the $\{1\bar{1}00\}$ faces. Further increase of the Sr content to 3.5% did not yield GaN crystals at all.

Kawamura et al. stated on the effect carbon (C) would have as an additive [24]. The growth rate was significantly increased above $20\,\mu m\,h^{-1}$ (even $30\,\mu m\,h^{-1}$ was reported [24]) because of suppressing theparasitic nucleation and stabilizing the
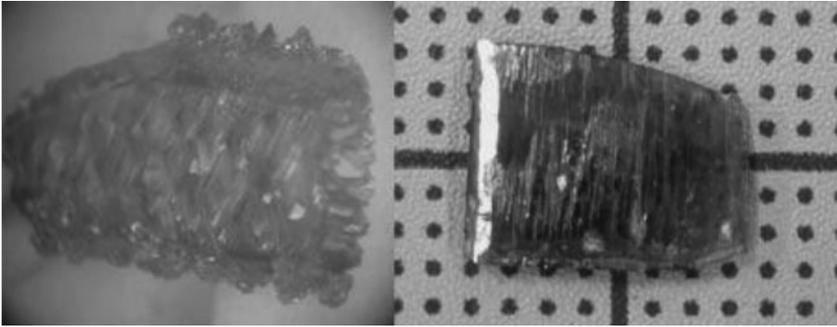
Fig. 11.4 Photograph of GaN produced on a-plane GaN templates in (**a**) the pure Na flux and (**b**) the Sr-added Na flux. (After [16]. Reprinted with permission. © 2007, The Japan Society of Applied Physics)

formation of the nonpolar m-face. Already 1 at% C at $T = 800\,°C$ would cause complete suppression of the parasitic nucleation. Moreover, seemingly C does not lead to strongly affect the C-level in the grown GaN. SIMS analysis revealed concentrations about $2 \times 10^{17}\,cm^{-3}$ which is the same amount as for those crystals grown under intentionally C-free conditions.

The transition metal additives chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), and nickel (Ni) have been employed [25]. Chromium resulted in coprecipitation of CrN single crystals whereas Mn, Fe, Co, and Ni rather had an effect on the GaN crystal morphology in that growth in the c- direction was enhanced with Ni illustrating the largest effect. Only Mn could be incorporated into GaN at concentrations up to 0.35 at% as detected by ICPMS.

Small crystals of the ζ-phase of Mn_2N could be prepared from an indium In–Na flux at 700 °C [26].

11.4.2 Growth Mechanism and Effect on Dislocation Population

Several factors do influence the defect formation and propagation during seeding and crystal growth, which was studied for the growth of GaN on (0001) MOCVD-GaN substrates [27]. Namely, this is the concentration of dislocations at the initial growth stage (nucleation of GaN islands on the substrate), which can be as high as this of the substrate typically for MOCVD layers $\leq 10^9\,cm^{-2}$. This is followed by the dislocation lines bending within a few micrometers above the interface of the substrate and the LPE grown GaN, which results in the low dislocation density of $10^3\,cm^{-2}$ [28] (Fig. 11.5).
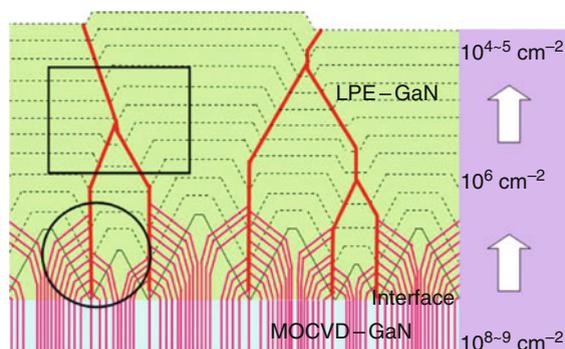
Fig. 11.5 Reduction of dislocations during the LPE growth of GaN on a MOCVD-GaN substrate by the Na-flux method. [12] (Reprinted with permission. © 2008, Elsevier Publishers.)

11.4.3   Solubility and Growth Rate

The Solubility of GaN is an essential parameter that would govern the crystal growth process. Kawamura et al. have investigated the solubility and reported that only 0.036 mol% of GaN can be dissolved in a flux of 27 mol% Ga and 73 mol% Na, while keeping the process running for 200 h at $T = 973$ K [12]. Adding Na to a Ga melt obviously improves the solubility of GaN and also allows applying lower pressure conditions. By comparison, Madar et al. reported a solubility of GaN in the pure Ga melt of only 0.008 mol% at $T = 1,473$ K and $p = 800$ MPa [29] and Karpinski et al. have observed a rise in the solubility to about 0.16 mol% at $T = 1,773$ K and $p = 1,600$ MPa [30].

The solubility of GaN can be expressed in terms of system pressure and temperature. A minimum pressure is required above which crystal growth of GaN is commencing. Above $T = 900$ K, Na is clearly promoting the dissolution of N in the Ga–Na melt. As a result, about 0.12 at% N dissolves at $T = 1,073$ K and $p = 0.75$ MPa in the flux of 27 mol% Ga and 73 mol% Na [9].

What is more, it was reported that the minimum pressure to grow GaN in the Ga–Na melt decreases until $T = 1,023$ K and after that increases. This phenomenon is explained in terms of the stronger rise of the solubility of GaN which exceeds that of N [9].

The growth rate depends on the thermal gradient between the substrate and the Na flux. Thermal convection inside the flux container is formed such way. Kawamura et al. recently reported a growth rate as large as $20\,\mu m\,h^{-1}$ in the direction of $\langle 0001 \rangle$ [20]. They furthermore found that a dwell time of about 20 h from starting the experiment until first growth appears is needed, which is mainly caused by the slow saturation of the Na flux with nitrogen until reaching a level of supersaturation that initiates the growth process on the substrate.

The control over parasitic nucleation is also a big challenge in the Na-flux method. It w as observed that they preferentially crystallize at the interface of the

Table 11.1 Properties of GaN crystals grown by the Na-flux method

	Self-seeded GaN			GaN grown on substrate
Lattice parameter	$a = 3.1903(3)$ Å [18] $c = 5.1864(6)$ Å [18]	$a = 3.1896(1)$ Å [4] $c = 5.1854(2)$ Å [4]	$a =$? $c = 5.1877$ Å [5]	/
XRC FWHM	/	/	25 arcsec (0004) 40–60 arcsec (0002) [9]	/
Impurities	/	/	/	$Na = 4.2 \times 10^{14}$ cm^{-3} [2] $C = 2 \times 10^{17}$ cm^{-3} [24]
Resistivity	/	/	0.04 Ωcm $(T = 110 - 350\,K)$ [5]	/
Carrier concentration	/	/	$1–2 \times 10^{18}$ cm^{-3} (RT), n-type [5]	/
Mobility	/	/	100 cm^2 V^{-1} s^{-1} (RT) [5]	/

liquid Na flux to the gas atmosphere, thus consuming a large fraction of the free N radicals needed to form the GaN on the substrate crystal. However, adding carbon (C) as additive would completely suppress the formation of parasitic GaN crystals and therefore support the growth of GaN on the substrate crystal [20].

11.5 Properties of GaN

There is only very limited data available on the structural and physical properties of GaN produced by the Na-flux method. Table 11.1 has listed the lattice parameter a and c, XRC FWHM, concentration of the impurities Na and C, electrical resistivity, carrier concentration, and carrier mobility as far as available.

Skromme at al. have investigated some optical properties of colorless prismatic GaN crystals grown by Yamane [31] by photoluminescence (PL), reflectance, and micro-Raman scattering. Raman scattering revealed an A_1(LO) phonon mode at 739 cm^{-1} indicating a free electron concentration around $2–3 \times 10^{17}$ cm^{-3} for 3–4 mm large platelets. Smaller platelets grown in a pyrolytic BN (pBN, purity > 99.9999%) crucible showed the A_1(LO) phonon mode at 733 cm^{-1}, implying a free electron concentration in the mid 10^{16} cm^{-3}. PL measurements disclosed a residual donor species with the binding energy of 33.6 meV, probably because of O_N. Residual zinc (Zn) acceptors have also been evidenced peaking around 2.9 eV with a broader peak in the low-temperature ($T = 1.7$ eV) spectrum. Other

impurities evidenced were Si and Mg, both at low levels. The yellow band around 2.2 eV, and usually associated with gallium vacancies, was rarely observed. In the low-temperature ($T = 1.7$ eV) PL measurement, the neutral donor-bound exciton (D^oX) emission was high in intensity with a small FWHM of only 2.2 meV. The authors concluded that the material was of excellent optical quality.

11.6   Industrialization Potential for the Na-Flux Method

The Na-flux method has proven the possibility to grow GaN crystals under relatively mild conditions with respect to pressure and temperature, i.e., $p \leq 10$ MPa and $600 \leq T \leq 900\,°C$, respectively. The growth rate of up to $30\,\mu m\,h^{-1}$ seems reasonable for industrial production purposes, particularly in the light of the intrinsically lower growth rates for growth techniques from the solution; refer also to Chaps. 7–10 and 12 in this book. The structural quality certainly can further be improved, especially in the view of single crystallinity and related grain boundaries for the wafer-sized area.

A critical issue in terms of industrialization of the Na-flux technology, essentially for all technologies considered to produce GaN crystals for GaN wafer fabrication, is the feasibility for upscaling in order to achieve a high crystal throughput, which would positively affect the cost per epi-ready GaN substrate. The ammonothermal technique seems to be most promising in this regard. In fact, the cost for an epi-ready GaN substrate is an increasingly important issue considered by device makers as it covers the largest fraction in the cost structure for a mass-produced GaN-based device. For a vast sector of GaN devices, the cost for an epi-ready GaN substrate has to compete with that for the widely used sapphire-based templates that can achieve high-quality GaN devices through sophisticated template technology in combination with epitaxial lateral overgrowth (ELO).

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