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# Gallium nitride bulk crystal growth processes: A review

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## Abstract

Optoelectrical and microelectronic devices involving gallium nitride have become a challenge but their development is limited because of a lack of suitable substrates. This paper deals with the crystal growth of gallium nitride, the processes leading to GaN bulk crystals being significantly expanded during the last decade (the ones involving GaN thin films or nanocrystallites are not studied in this review). The main reviewed routes are: (i) the high pressure nitrogen solution growth (H.P.N.S.G.), (ii) the Na flux method, and (iii) the ammonothermal crystal growth.

*Keywords:* GaN; Crystal growth; Nitrides; Functional materials

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## 1. Introduction

Wide band gap semiconductors such as gallium nitride present a large interest for many applications in opto- and microelectronic [1,2]:

- white or color light emitting diodes (LEDs) for color displays or street lighting,
- blue or violet laser diodes (LDs) for laser printing or optical storage of data,
- UV detectors for identification or guidance of missiles,
- high power-high frequency transistors for radars or communication.

The currently available devices use GaN deposited by epitaxy on different substrates (reviewed in [3]) because of the lack of GaN substrates. The resulting thin films exhibit large defects concentrations due, in particular, to the difference of thermal expansion coefficient between such substrates and GaN. Then only devices mentioned above are available: LEDs since 1995 and LDs more recently. The others need some improvements of GaN films quality before any commercialization. Homoeptaxy could solve this difficulty as underlined in various studies [4–8]; thus, the elaboration of GaN single crystals has been the challenge of many research works during these last 20 years.

Due to the high covalency of GaN [binding energy of the gallium nitrogen bond  $E \approx 9.12$  eV/atom] the decomposition pressure ( $P_M$ ) at the melting point ( $T_F \sim 2500$  °C, Van Vechten [9]) is extremely high ( $P_M \sim 4.5$  GPa, Karpinski et al. [10]). For pressure values below  $P_M$ , gallium nitride does not melt and thus decomposes. At atmospheric pressure for example, gallium nitride is stable until 1200 K and it can be stabilized at higher temperature by enhanced pressures [10]. Consequently,

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in such a case, the standard techniques of crystal growth generally used for the elaboration of semiconductor wafers (Bridgman, Czochralski, Verneuil) cannot be developed. The congruent melting of gallium nitride has only been achieved very recently by Utsumi et al. [11]. This technique does not lead presently to large crystals ( $<100\ \mu\text{m}$ ), the experimental conditions (6 GPa, 2200 °C) being a limiting technical development for developing a production.

Due to the gallium nitride decomposition, only few methods have been developed for preparing GaN bulk crystals.

- (i) The larger GaN crystals (platelets with a surface exceeding now  $100\ \text{mm}^2$ ) have been elaborated through the high pressure nitrogen solution growth (H.P.N.S.G.), developed since 15 years at Warsaw (Poland) [Porowski [12]]. High nitrogen pressure and high temperature conditions (1–2 GPa, 1400–1500 °C) are then required for the conversion of metallic gallium in gallium nitride.
- (ii) The Na flux method has been introduced at Sendai (Japan) in the middle of the 1990's by Shimada and co-workers [13] and leads to smaller GaN crystals than H.P.N.S.G. Lower pressure and temperature conditions (5–10 MPa, 700–800 °C) are used, sodium acting as a catalyst for the dissociation of nitrogen molecules.
- (iii) Lastly, the ammonothermal crystal growth (solvothermal process using  $\text{NH}_3$  as solvent) has not allowed the preparation of large GaN crystals yet but seems to be a promising technique for the preparation of crystals with appropriate size and crystalline quality. Gallium nitride being almost insoluble in ammonia, mineralizers such as the mixture  $[\text{KI} + \text{KNH}_2]$  or more recently  $\text{KN}_3$  have been used by Kolis et al. [14,15].

## 2. The high pressure nitrogen solution growth process

### 2.1. First research works involving H.P.N.S.G. process

The H.P.N.S.G. originates from research works realized by Karpinski et al. [16,17] in the early 1980s about gallium nitride stability up to 2300 °C and 6 GPa. Its aim was to specify the work of Madar et al. [18] carried out in the middle of the 1970s which was limited to 1200 °C and 0.8 GPa. Gallium nitride bulk crystals which size could reach 1 mm were elaborated in vapor phase at 1200 °C and 0.8 GPa. The nitrogen solubility in gallium was small (about 0.01%) in these conditions of pressure and temperature explaining the very low growth rate observed ( $1\ \mu\text{m}\ \text{day}^{-1}$ ) [16]. Moreover, this study drew up the nitrogen ( $\text{N}_2$ ) equilibrium pressure over GaN versus temperature ( $\sim 1\ \text{MPa}$  at 1000 °C,  $\sim 2\ \text{GPa}$  at 1700 °C or  $\sim 4\ \text{GPa}$  at 2300 °C) [17].

As proposed by Van Vechten [9], the melting temperature was over 2300 °C at 6 GPa. Furthermore, a great difference between the experimental values and the calculated ones, for an ideal gas, were observed. For instance, the nitrogen equilibrium pressure over GaN at 1700 °C was only 2 GPa whereas it should be 6.5 GPa for an ideal gas. The effect of the nitrogen non-ideality was not detected by Madar et al. due to the limited  $P, T$  experimental domain [18]. Since pressure and temperature about 2 GPa and 1700 °C could be carried out experimentally, this experimental conditions could help the crystal growth of GaN [17]. Moreover, the solubility of nitrogen in liquid gallium was evaluated to 1% at 1500 °C and 1.6 GPa during GaN crystal growth through vapor phase [17]. The growth rate of GaN layers (on a sapphire substrate) was then increased to about  $1\text{--}10\ \mu\text{m}\ \text{h}^{-1}$ .

In 1991, Grzegory et al. [19] studied the solubility of nitrogen in liquid gallium versus pressure and temperature. This solubility was improved with pressure and temperature, from  $\sim 0.01\%$  at

$\sim 300$  MPa and  $\sim 1600$  °C to  $\sim 0.5\%$  at  $\sim 1.45$  GPa and  $\sim 1850$  °C for instance. The extrapolation of the solubility curve versus temperature to a nitrogen molar fraction of 0.5 (corresponding to GaN) shows that the melting temperature is about 2500 K, which is in reasonable good agreements with Van Vechten's calculation [9]. The high increase of the solubility with pressure and temperature implied that high pressure synthesis processes could allow quite important growth rates.

## 2.2. Improvements of the H.P.N.S.G. process

### 2.2.1. Experimental device and crystal growth

High pressure–high temperature (HP–HT) route was then developed by Porowski and co-workers [12,20–22]. The experiments were realized in a high pressure chamber containing a furnace of inside diameter 14 mm (for temperatures up to 1500 °C) or 10 mm (for temperatures up to 1700 °C), with a BN vessel partially filled with metallic gallium. After heating in vacuum in order to eliminate oxygen, the vessel was filled with pure nitrogen gas, compressed and heated. Temperatures were stabilized with a minimum precision of 1°. The pressure was ranged from 0.8 to 1.7 GPa, the temperature from 1300 to 1700 °C, the thermal gradient  $\Delta T$  between the top and the bottom of the vessel from 30 to 100 °C, and the experimental duration from 5 to 24 h [10]. The resulting GaN crystals were separated from the metallic gallium by a chemical treatment with boiling nitric acid [20].

### 2.2.2. Crystal growth mechanism

The crystallization mechanism was typically driven by solid diffusion [22] in which a GaN polycrystalline film was firstly formed on the liquid gallium surface no seeds being introduced before the experiments. Metallic gallium appeared to help the dissociation of the nitrogen molecule in atomic nitrogen, leading to a lower potential barrier (3.5 eV) while the  $N_2$  molecule bonding energy is 4.9 eV/atom. Gallium nitride crystallites were then formed on the surface of the liquid gallium. These crystallites were then dissolved in melt gallium and atomic nitrogen was transported toward the coldest part of the solution. Nitrogen supersaturation was supplied by the thermal gradient, its solubility decreasing with temperature (cf. Section 2.1). The more the gradient value was important, the more the supersaturation was high. Moreover, there was no GaN nucleation within the solution, even at high supersaturation values [23].

Crystals morphology depended on the experimental conditions: for conditions out of equilibrium (the nitrogen pressure value being far from the determined equilibrium one [17]) hexagonal prism shape (elongated along  $c$ -axis) was observed whereas for those close to equilibrium conditions hexagonal plate shape (perpendicular to  $c$ -axis) was resulting. Generally, the largest dimension was along  $[1\ 0\ \bar{1}\ 0]$  and the smallest one along  $[1\ 1\ \bar{2}\ 0]$ , the thickness being hundredth of the length [10]. For high growth rate values ( $\sim 1$  mm  $h^{-1}$  in  $[1\ 0\ \bar{1}\ 0]$  direction), crystals had an unstable growth and present skeletal, hollow or dendritic shape [22]. These high growth rates were obtained for the highest values of nitrogen supersaturation in gallium solution. In particular, when the crystal size was reaching the vessel one, a non-uniform distribution of nitrogen was observed. The layer-by-layer mechanism was thus disturbed, inducing a bad crystalline quality through the formation of defaults in the crystal [12].

### 2.2.3. Properties of the resulting crystals

Bulk crystals obtained in equilibrium conditions were usually transparent with a light yellow coloration and presented the wurtzite type structure [12,21]. Scanning tunneling microscopy (STM) were realized on a hexagonal plate (2.5 mm  $\times$  2.5 mm) elaborated at 1 GPa and 1400 °C during 20 h. The  $(0\ 0\ 0\ 1)_{Ga}$  face was smooth, with steps between 20 and 40 Å only while the  $(0\ 0\ 0\ \bar{1})_N$  one was rough with pyramids of 100–300 Å. Moreover, precipitates constituted of gallium were observed on

the  $(000\bar{1})_N$  face. The  $(0001)_{Ga}$  face was chemically active while the  $(000\bar{1})_N$  one was not. The crystalline quality was evaluated by X-ray diffraction (XRD) [12]. The full width at half maximum (FWHM) of the  $(0004)$  peak, with Cu  $K\alpha$  source, was about 20–30 arcsec for crystals with size below 1 mm and up to 40–50 arcsec for larger crystal size (1–3 mm). This enlargement was associated with a splitting of the peak attributed to low angle boundaries for GaN crystal. The theoretical FWHM value was estimated about 12 arcsec for an ideal crystal [12].

Until the middle of the 1990s, the optimum size of the obtained crystals through this process was limited to 4–6 mm. An increase of the vessel volume, associated to longer duration should allow an increase of the crystal size up to 10 mm [22,24,25].

### 2.3. Optimizations of the H.P.N.S.G. process

#### 2.3.1. Experimental device and crystal growth

The most recent experiments were performed in a high pressure chamber with a large volume ( $1500\text{ cm}^3$ ) and an internal diameter close to 30 mm using a BN crucible. The maximum pressure value reached 2 GPa [26,27]. Temperature and pressure could be, respectively, adjusted with a precision over  $0.02\text{ }^\circ\text{C}$  (in all the heating zones) and 1 MPa, respectively. The nitrogen supersaturation in the gallium solution was generated by a thermal gradient  $\Delta T$  with a value between 2 and  $20\text{ }^\circ\text{C cm}^{-1}$ . Greater GaN bulk crystals were then elaborated, their size depending on the BN crucible volume. They were transparent and colorless [26]. Grzegory et al. [28] proposed an hypothesis for the limitation of the crystal size versus the BN crucible one. An increase of the experimental duration beyond 150 h did not allow an enhancement of the crystal size. If the crystal was too large – for a given vessel size – nitrogen transport was not fast enough to ensure, in the gallium solution, a uniform concentration corresponding to equilibrium, for the hot zone of the vessel. Moreover, the convection movements in the crystallization zone could be reduced by the crystals formed into the solution. The deposit conditions could then be changed for the rest of the solution [28].

#### 2.3.2. Properties of the crystals elaborated through the optimized H.P.N.S.G. process

The resulting crystals were characterized by XRD. The FWHM of  $(0004)$  peak, for a Cu  $K\alpha$  source, was about 20–30 arcsec for crystals up to 3 mm (against 1 mm before) and up to 40–50 arcsec for 12 mm ones. Their crystalline quality was evaluated more precisely with the determination of the lattice parameters on the whole crystal volume [29]. For crystals exceeding 2 mm, the parameters  $a$  and  $c$  were slightly larger (0.01%) on the  $(0001)_{Ga}$  face than on  $(000\bar{1})_N$  one. This difference corresponded to a curvature of the plates, which radius was evaluated to 1.5 m. The parameters raise was probably originating from a greater growth rate on N face, in Ga rich conditions, inducing an increase of point defects (Ga antisites, N vacancies, Ga interstitials). The most probable point defects in these crystals are gallium vacancies due to their low formation energy even in gallium rich crystallization conditions [30]. Their concentration was about  $10^{18}\text{ cm}^{-3}$ , as shown by positron annihilation. They were negatively charged and their concentration was correlated to the intensity of the yellow luminescence (YL) in the photoluminescence spectra (PL). The PL spectra of GaN crystals (non-intentionally doped) indeed exhibited a peak corresponding to the near band-edge emission at  $\sim 3.4\text{ eV}$ , as well as a strong broad band at 2.3 eV corresponding to YL [25]. The last one is usually attributed to transitions between residual deep donor levels and deep acceptor levels at  $\sim 1\text{ eV}$  above the valence band. As gallium vacancies induced a deep acceptor level at about 1.1 eV above the valence band [30] they were probably generating the strong yellow band.

The grown-in extended defects in H.P.N.S.G. crystals were studied through various techniques: X-ray projection topography [31], transmission electron microscopy (TEM), convergent beam

electron diffraction (CBED) [32] and chemical etching [33]. X-ray topography measurements showed that dislocations were perpendicular to the growing lattice plane [31] and CBED that there was neither etch-channel nor extended dislocation along the  $c$ -axis in the plates [32]. Growth polarity direction was playing a key role in the formed defects and in the roughness of the surface. These techniques could explain the value of the dislocations density: it did not exceed  $2 \times 10^2 \text{ cm}^{-2}$  in crystals elaborated through H.P.N.S.G. [31–33].

Non-intentionally doped crystals exhibited however a high n-type conductivity with a free electron concentration of  $5 \times 10^{19} \text{ cm}^{-3}$ , a resistivity about  $10^{-3}$ – $10^{-2} \Omega \text{ cm}$  and a mobility of  $60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [27]. These electrons were probably originating from the oxygen atoms substituting nitrogen. A high oxygen concentration (about  $10^{18}$ – $10^{19} \text{ cm}^{-3}$ ) was indeed evidenced through secondary ion mass spectrometry (SIMS) characterizations. Moreover, unlike nitrogen, the dissociation of the oxygen molecule on the surface of the gallium solution is a process without energy barrier that favors its incorporation into gallium nitride during the crystal growth [26].

Furthermore, infra-red reflectivity and micro-Raman scattering revealed a gradient of free carriers concentration along  $c$ -axis in H.P.N.S.G. undoped crystals [31]. The free electrons concentration is always higher for the  $(000\bar{1})_{\text{N}}$  face ( $10^{20} \text{ cm}^{-3}$ ) than for the  $(0001)_{\text{Ga}}$  one ( $5 \times 10^{19} \text{ cm}^{-3}$ ). Moreover, its evolution was not linear along  $c$ -axis but presented an abrupt change from high to low electron concentrations. In order to explain this phenomenon, an hypothesis was made about the crystal growth process: assuming that during the growth, oxygen impurities were incorporated in the lattice, more in the  $[100\bar{1}]$  direction than in the  $[0001]$  one. In the  $[100\bar{1}]$  direction, one oxygen atom is indeed linked to three gallium atoms, which is a more stable situation than the bonding to only one gallium atom as in the  $[0001]$  direction [34].

#### 2.4. Elaboration of doped crystals through the H.P.N.S.G.

For p-doping, beryllium or magnesium were added (0.2–0.5%) to the metallic gallium before the crystal growth [35]. The crystals doped with Be or Mg exhibited almost the same morphology than non-doped ones, but their physical properties were obviously very different.

##### 2.4.1. Magnesium doping

With magnesium doping, the thickness of the plates was slightly larger and the lattice parameters were slightly smaller than these of undoped ones. Moreover, XRD studies showed that the  $(0002)$  FWHM was about 18–25 arcsec for almost all crystals, whatever their size, and that there was no curvature as identified for non-doped crystals [36].

No gallium vacancy was detected through positron annihilation and the PL spectrum did not contain the strong yellow band. Moreover, PL spectrum showed a large band (0.2 eV) centered at 3.1 eV ever encountered in Mg doped thin films: and originating from magnesium atoms substituting gallium ones. At a concentration about  $10^{19} \text{ cm}^{-3}$ , lattice parameters decrease theoretically of 0.1%. Magnesium impurities compensate residual donors and probably block their formation during crystal growth. This low dislocation density determined through TEM ( $10 \text{ cm}^{-2}$ ) and chemical etching ( $10$ – $100 \text{ cm}^{-2}$ ) confirmed this evolution [37].

Incorporation of Mg impurities induced drastic decrease of free electrons concentration in comparison with non-intentionally doped crystals: Mg doped crystals exhibited a resistivity about  $10^4$ – $10^6 \Omega \text{ cm}$  at 300 K. In some experiments, GaN:Mg crystals became p-type semiconductors, the activation energy (between valence band and acceptor levels) being of the order of 150 meV at temperature slightly over 300 K. Electric activation of Mg acceptor was then not very efficient, i.e. that the valence band was containing a very low hole concentration [36].

Electrical properties were studied versus annealing (between 300 and 750 °C) [38]. The proposed model contained two defect levels: one was shallow and the other deep (respectively at 0.1 and 0.9 eV from the valence band), these levels being compensated by shallow oxygen donors. The deep levels should be responsible for the immobilization of the Fermi level into non-treated samples and at the beginning of the annealing at low temperature. The Mg shallow acceptor levels (at 0.1 eV from the valence band) should be created during the annealing at low temperature (in small amounts however) and should become dominant. High temperature annealing processes could lead to an activation barrier being twice at low temperature, which could cause the formation of a large number of deep centers [38].

#### 2.4.2. Beryllium doping

No change in the structure of the polar faces or in the thickness of the crystals was observed in comparison with non-doped crystals [39]. The resistivity of these crystals could be up to  $10^6 \Omega \text{ cm}$  at 300 K. GaN:Be crystals were highly resistive, with an activation energy of 1.46 eV at temperatures reaching 1000 K. With Be incorporation, there was thus a total elimination of free electrons concentration noticed in non-intentionally doped crystals. The holes induced by the beryllium (acceptor) were indeed compensating the electrons from the oxygen (donor). Their properties were not depending on the annealing. PL spectra were dominated by a very strong yellow band as the crystals presented a high concentration of Ga vacancies ( $10^{18} \text{ cm}^{-3}$ ) [40]. In order to explain this behavior, the hypothesis was that GaN:Be crystals were p-type throughout their growth, Be atoms occupying interstitial positions in GaN lattice. During the cooling, Be atoms diffused towards the Ga vacancies [39].

### 2.5. Crystal growth from seeds according to the H.P.N.S.G. process

#### 2.5.1. Crystal growth using GaN based seeds

The first experiments of crystal growth from seeds were realized through H.P.N.S.G. [40,41]. Two crystallographic directions were investigated: one corresponding to the smallest growth rate ( $[0\ 0\ 1]$ ) and the other leading to the highest one ( $[1\ 1\bar{2}\ 0]$ ).

Crystal growth from Mg-doped seeds on the  $(0\ 0\ 1)$  face was realized through H.P.N.S.G. with a very high thermal gradient ( $100 \text{ }^\circ\text{C cm}^{-1}$ ) due to the very low growth rate along the *c*-axis [41]. The substrate was first covered at 1500 K with liquid gallium at low nitrogen pressure and then the pressure was increased up to the experimental crystal growth one (1.5–2 GPa). In only 50–100 h, a wurtzite type GaN hillock with a diameter about 6 mm and a thickness about 200  $\mu\text{m}$  was obtained on the crystal that was used as a seed. The growth rate was between 4 and 8  $\mu\text{m h}^{-1}$ , against 1–2  $\mu\text{m h}^{-1}$  for H.P.N.S.G. with spontaneous nucleation. The XRD FWHM were the same as these of the GaN seed. The formation of roughness on the Ga polar surface was suppressed by means of a positive thermal gradient perpendicularly to the growth front. The growth mechanism should consist in the propagation of macrosteps from the hillock center, the steps near the center corresponding to a higher supersaturation zone (with higher growth rates) than these closer to the step wall [41].

Gallium nitride crystal growth along  $[1\ 1\bar{2}\ 0]$  was performed from a fragment (about 1 mm wide and 4–5 mm long) of GaN crystal elaborated by classical H.P.N.S.G. [40]. As previously, the substrate was covered with liquid gallium at high temperature and low pressure. The lateral dimension of the elaborated crystal was similar to this of the seeds whereas the perpendicular dimension depended on the crystal growth duration. The introduction of seeds in the vessel controlled the position of the GaN crystals during H.P.N.S.G. experiments [40].

### 2.5.2. *H.P.N.S.G. crystal growth of GaN on templates (sapphire/GaN) or substrates (GaN/sapphire)*

The progress in blue laser diodes and UV light sources is still limited by the lack of high quality and large (1–2 inches) GaN wafers and by the density of defects.

Recently in order to improve the thickness of GaN crystals, the crystallization of GaN in *c*-direction on sapphire/GaN templates was examined by Bockowski et al. [42]. Two main factors seem responsible for GaN growth in *c*-direction: for short time the growth rate is mainly controlled by nitrogen transport, for longer duration the surface kinetics factor was predominant. Then the same Research Group evaluated the high pressure solution growth of GaN on GaN/sapphire substrates, patterned in GaN parallel stripes. The stripes grow in lateral and *c*-directions. The dislocation densities in the laterally overgrown areas have been found in the range  $5 \times 10^5$  to  $10^6 \text{ cm}^{-2}$  [43].

Crystallographic and chemical inhomogeneities occurring in GaN single crystals (grown by high pressure method), homoepitaxial layers and quasi-bulk thick epitaxial layers (MOCVD and HVPE) have been recently investigated by Weyher [44]. Among the defects observed in HP-grown GaN single crystals, the most important for the crystalline quality of homo-epitaxial structures are micro-defects.

## 2.6. *The pressure-controlled solution growth (P.C.S.G.) process*

Inoue et al. [45–47] recently proposed another process also based on the conversion of liquid gallium into GaN under high nitrogen pressure at high temperature: the pressure-controlled solution growth.

### 2.6.1. *Description of the P.C.S.G. process*

Preliminary experiments showed the possibility to elaborate GaN crystals without any thermal gradient under experimental *P*, *T* conditions closed to those of the H.P.N.S.G., an nitrogen overpressure inducing the N supersaturation in liquid gallium [45]. The experimental device consisted in a high pressure furnace (for pressure up to 0.98 GPa and temperature up to 2000 °C) including a pyrolytic BN vessel (38 mm diameter). Firstly the equilibrium pressure was studied through experiments carried out at 1450 °C under a nitrogen pressure between 0.69 and 0.98 GPa: their results were in good agreement with those of Karpinski et al. [10]. The growth rate was then determined (i) versus temperature (1350–1600 °C) at 0.98 GPa with a gallium weight of 420 g and (ii) versus gallium weight (10–420 g) at 1475 °C and 0.98 GPa. The growth rate increased with temperature from 1350 to 1475 °C, its values being zero below 1350 °C and above 1525 °C: thus, it was maximum at 1475 °C. Moreover, the growth rate was largely decreasing with the gallium weight which was consistent with a diffusion process for the crystal growth [45].

Gallium nitride crystals were then grown at 1400–1500 °C and 0.98 GPa. A small thermal gradient (about 1 °C) was applied in order to select the part of the vessel where the crystals were elaborated [45]. No information was given about the overpressure applied during the experiment. After experiment, the furnace was cooled down to room temperature during 2 h. The resulting crystals, as hexagonal platelets, were yellowish and transparent with a diameter usually about 7 mm (at growing temperature of 1450 °C for 9 h), reaching 10 mm mainly near the surface of the liquid gallium. XRD evidenced that the normal axis of the platelets was the *c*-axis of the wurtzite structure. The dislocation density was found to be under  $10^6 \text{ cm}^{-2}$  through TEM observations and the free carrier concentration about  $10^{20} \text{ cm}^{-3}$  through PL analysis [45]. The dislocation density and the free carrier concentration were larger than those of crystals elaborated by H.P.N.S.G., probably because of the small durations of the crystal growth experiments inducing high growth rates and thus defaults.

### 2.6.2. Improvements of the P.C.S.G. process

The size of the surface area of the GaN platelets was then studied versus the supersaturation, i.e. the rate of increase of  $N_2$  pressure [46]. When the equilibrium pressure of 0.98 GPa at 1475 °C was reached, the  $N_2$  pressure was increased with a rate up to 300 MPa  $h^{-1}$ , for durations from 0.5 to 16 h. Thus, GaN single crystals were elaborated at rate values from 8 to 293 MPa  $h^{-1}$ , their surface area decreasing from 120 to 80 mm<sup>2</sup> with reducing rate. This phenomenon was explained by the raise of the number of nuclei when the supersaturation was high, that corresponded to a large rate of increase of  $N_2$  pressure, above 50 MPa  $h^{-1}$ . Moreover, the morphology of the crystals was also affected: at lower rate (8 MPa  $h^{-1}$ ) the GaN platelets were flat and smooth whereas from 12 MPa  $h^{-1}$  the surface presented growth steps arranged around an hexagonal axis. To sum up, low rate allowed the elaboration GaN crystals with a stable morphology corresponding to a slow growth [46].

The crystals exhibited a quite good crystalline quality with the (0 0 0 2) FWHM value [X-ray diffraction peak Cu  $K\alpha 1$  source] usually about 120 arcsec and a dislocation density below  $10^5$  cm<sup>-2</sup> as estimated by TEM observations. The PL spectra of the most flat platelet contained a very weak yellow band at 2.3 eV compared to the band-edge one at 3.5 eV [46].

### 2.6.3. First optimizations of the P.C.S.G. process

A new larger high pressure furnace was used in order to grow larger GaN crystals: the diameter and the height of the processing volume were then increased from 40 and 100 mm to 60 and 150 mm, respectively [47]. The maximum values of experimental pressure and temperature were 1.0 GPa (with accuracy of 0.01%) and 1600 °C (with a precision of 1.0 °C), respectively. Several (10) BN vessels (52 mm diameter), charged with gallium, were placed simultaneously in the HP furnace. The optimization of the experimental crystal growth conditions was still in progress but a crystal with a size up to 25 mm (surface area over 300 mm<sup>2</sup>) was grown at 1475 °C and 1 GPa for 16 h with a rate of increase of  $N_2$  pressure about 69 MPa  $h^{-1}$  [47]. It was a yellowish transparent hexagonal platelet with macrosteps and its crystalline quality seemed to be equivalent to the one of the crystal elaborated in the previous study at high rate [46].

## 3. Processes using a Na flux

### 3.1. First step of the Na flux development

Several works dealing with GaN crystal growth were then carried out by Yamane et al. at the end of the 1990s and a process based on a sodium flux was developed [13,48,49]. As they were working on the elaboration of alkali nitrides they did not succeed in the synthesis of the mixed nitride of sodium and gallium, discovering however that GaN could be obtained in sodium.

#### 3.1.1. Experimental device

For those experiments, sodium azide and gallium were introduced under argon atmosphere into a stainless steel tube, which was then sealed and placed in a furnace. Above 300 °C,  $NaN_3$  decomposed into Na and  $N_2$ , and supplied high purity nitrogen and sodium, this one being eliminated by washing with ethanol at the end of the reaction. The experiment were performed at a temperature between 600 and 800 °C under a pressure between 5 and 10 MPa for a duration from 24 to 96 h and with a  $r_{Na}$  ratio between 0.2 and 0.8 [the parameter  $r_{Na}$  being defined as the molar ratio of sodium ( $r_{Na} = n_{Na} / [n_{Ga} + n_{Na}]$ ] [13]. Wurtzite-type gallium nitride was observed for high values of  $r_{Na}$ . An increase of the pressure or of the temperature parameter shifted the GaN domain to larger values of the ratio  $r_{Na}$ .

For the highest  $r_{\text{Na}}$  values, gallium nitride was synthesized as a dark colored fine powder whereas transparent crystals were observed for lower ones. GaN crystals exhibiting a size above 0.1 mm were prepared in 24 h in the following experimental conditions:  $P = 10$  MPa,  $T \geq 700$  °C and  $0.3 \leq r_{\text{Na}} \leq 0.7$ . The largest ones were greenish and transparent hexagonal platelets 0.5–1 mm (for a duration of 24 h). The color of those crystals was attributed to nitrogen vacancies or impurities such as oxygen. Moreover, a raise in the duration led to an increase of the crystal size: for instance, 0.2 mm transparent and colorless hexagonal platelets were elaborated in 40 h at 600 °C and 10 MPa with  $r_{\text{Na}} = 0.64$  whereas their size was only 0.1 mm in 24 h in the same conditions [13].

The effect of the  $r_{\text{Na}}$  ratio on the GaN crystals morphology was further studied, following a similar technique to the one described previously, the experimental conditions being 750 °C, 10 MPa and 100 h [48]. The largest crystals were generally obtained for low  $r_{\text{Na}}$  values ( $0.31 \leq r_{\text{Na}} \leq 0.38$ ): these bulk or platelet crystals were transparent and colorless or colored (orange or blue), with a maximum size of 0.8 mm  $\times$  0.5 mm  $\times$  0.5 mm. At higher  $r_{\text{Na}}$  values ( $r_{\text{Na}} = 0.47$ ), crystals in shape of hexagonal platelets were elaborated with an average size about 0.2 mm  $\times$  0.2 mm  $\times$  0.2 mm, the largest one reaching unusually 1 mm long. They grew perpendicular to the inner wall of the tube, just above the surface of the Na–Ga melt. When the  $r_{\text{Na}}$  value increased, the crystals morphology changed from prismatic to platelet; at very high  $r_{\text{Na}}$  ratio, only GaN granules were observed [48].

### 3.1.2. Properties of resulting crystals

Prisms and platelets, elaborated for  $r_{\text{Na}}$  ratio of 0.38 and 0.47, were characterized by electric measurements [48]. Their resistivity was, respectively 0.01 and 0.1  $\Omega$  cm at 300 K and was almost constant in the range 150–300 K. The prisms presented a free electrons concentration of  $5 \times 10^{20}$  cm<sup>-3</sup> and a mobility of 100 cm<sup>2</sup> V<sup>-1</sup> cm<sup>-1</sup>, whereas these values were  $7 \times 10^{20}$  cm<sup>-3</sup> and 9 cm<sup>2</sup> V<sup>-1</sup> cm<sup>-1</sup> for the platelets. As observed through X-ray diffraction, the platelets are characterized by a smooth face and a rough one with small hillocks, corresponding, respectively to the N terminated (000 $\bar{1}$ ) and the Ga terminated (0 0 0 1) faces. These results were opposite to those for H.P.N.S.G. platelets observed by Leszczynski et al. [29] (Section 2.2.3), certainly resulting from a different reactional mechanism [48].

### 3.2. Improvements of the Na flux process

The crystal growth of GaN in the previously described experiments was limited on several points, which induced three main improvements:

- (i) The stainless steel tube used as a container for the Na–Ga melt during these experiments was not exactly adapted because it was reacting with the melt. A boron nitride crucible was then introduced in the stainless steel tube in order to separate the reagents from the tube. [50].
- (ii) The experimental pressure was depending on the  $r_{\text{Na}}$  ratio, nitrogen being provided by the thermal decomposition of NaN<sub>3</sub>. The range of the experimental parameters that could be explored was thus restricted. Therefore, the control of the  $r_{\text{Na}}$  ratio was realized independently of the nitrogen content adding metallic sodium to sodium azide [51].
- (iii) In the previous experiments, the pressure was decreased with time down to few MPa because of the consumption of nitrogen. The duration of the crystal growth experiments was then limited as well as the size of the resulting crystals. Therefore, a constant pressure was maintained through a regular supply of nitrogen during the experiments, whose duration could be extended [52].

### 3.2.1. Experimental device and crystal growth

According to the improvements explained above the experiments were realized as described below:

- (i) For isolating the reagents from the stainless tube, they were introduced under inert atmosphere into a BN vessel that was then placed in the stainless steel tube before sealing. Experiments were realized in the following experimental conditions:  $T = 650\text{ }^{\circ}\text{C}$ ,  $t = 300\text{ h}$  and  $0.15 \leq r_{\text{Na}} \leq 0.75$  (the corresponding pressure was not specified) [50].
- (ii) For controlling  $r_{\text{Na}}$  value independently from the pressure, the experiments presented a single change compared with the previous ones (Section 3.1.1): sodium azide was added to metallic sodium and gallium in the stainless steel tube. GaN crystals were obtained at  $650\text{--}840\text{ }^{\circ}\text{C}$  during  $6\text{--}300\text{ h}$  for  $r_{\text{Na}}$  values between 0.42 and 0.52 [51].
- (iii) For the regulation of nitrogen pressure in the experiments, sodium azide was replaced by metallic sodium. Indeed, in the previous experiments, the gaseous nitrogen was obtained by the sodium azide decompositions, which also provided sodium. As, in this case,  $\text{N}_2$  was continuously introduced in the stainless vessel during the reaction, only sodium was required as previous reagent. The explored experimental conditions were the following:  $750\text{ }^{\circ}\text{C}$ , 5 MPa and 200 h for a  $r_{\text{Na}}$  ratio in the range 0.40–0.67 [52].

Generally, the same observations could be made for all these experiments concerning the influence of the  $r_{\text{Na}}$  value: the lower it was, the more gallium nitride was formed and the more the growth rate decreased. Crystals with platelet and pyramidal shapes were obtained, respectively, on the vessel wall and on the inner face of the polycrystalline layer that was formed at the surface of the Na–Ga melt, i.e. the face in contact with the liquid. Moreover, GaN crystal growth within the melt was revealed for some cases.

During the experiments with a regulation of the nitrogen pressure (5 MPa), 3 mm transparent and colorless hexagonal platelets were elaborated on the polycrystalline GaN layer, for a  $r_{\text{Na}}$  ratio equal to 0.60. They were larger than those obtained without the pressure regulation, with a maximum size about 1–2 mm. The tube wall and the bottom of the vessel also presented smaller GaN crystals (about 0.5–0.7 mm), mainly transparent and colorless.

### 3.2.2. Reactional mechanism

Yamane et al. described the crystal growth mechanism in the reactional tube [51]. Firstly, a polycrystalline layer should be synthesized on the surface of the Na–Ga melt, by the reaction of liquid gallium and nitrogen provided by the thermal decomposition of sodium azide. Then, GaN crystals with a prismatic or pyramidal morphology grew below the polycrystalline layer. Prismatic crystals and hexagonal platelets should also be formed on the wall tube, Na–Ga melt wetting them above the liquid surface. The reaction rate was improved by an increase of the temperature or of the sodium ratio in the Na–Ga melt. The authors did not propose any hypothesis for the change in the observed morphologies versus the values of the  $r_{\text{Na}}$  ratio and/or the place where the crystals were growing. The larger platelets were elaborated for a  $r_{\text{Na}}$  value of 0.60: in these conditions, the growth rate was acceptable and the polycrystalline layer was formed more slowly (this one being able to prevent or reduce nitrogen supply in the Ga–Na melt) [52].

A mechanism was proposed in order to explain why the experimental  $P$ ,  $T$  conditions were lower in Na flux experiments than that observed with the H.P.N.S.G. [51]. Generally, nitrogen does not react with gallium below  $950\text{ }^{\circ}\text{C}$  [18] because of the high bonding energy of the nitrogen molecule. However, it was observed that nitrogen and gallium reacted far below this value: sodium probably

acted as a catalyst for the reaction between Ga (or a Ga–Na intermetallic) melt and  $N_2$ . Sodium is indeed one of the alkali metals that can easily give up an electron, its ionization potential being quite low ( $196 \text{ kJ mol}^{-1}$ ). Yamane et al. [51] proposed that the nitrogen molecules, which were absorbed on the Na–Ga melt, could capture the electrons from Na, those one filling the first empty orbitals of the nitrogen molecules. Those orbitals being antibonding ( $2\pi_g^*$ ), nitrogen bonds should then be weakened favouring their dissociation in two negatively charge nitrogen atoms. There is no sodium nitride or mixed nitride between gallium and sodium and the nitrogen solubility is very low in Na melt ( $7.1 \times 10^{-9}\%$  at  $600 \text{ }^\circ\text{C}$ ). Gallium should thus be the only element able to catch nitrogen, forming then a nitride. Gallium atoms in Na–Ga melt near the interface should form species containing or not sodium atoms ( $Na_x[GaN_y]$ ) [51].

### 3.2.3. Physical and chemical properties of elaborated crystals

A 1 mm transparent and colorless hexagonal platelet, elaborated for a  $r_{Na}$  value 0.60, was characterized through XRD and then electrical and cathodoluminescence (CL) measurements [52]. The FWHM of the (0 0 0 4) peak was 25 arcsec and the  $c$  lattice parameter 5.1877 Å. Its resistivity closed to  $0.06 \text{ } \Omega \text{ cm}$  was nearly constant in the range 110–300 K. Its conductivity was n-type with a free carrier concentration about  $1\text{--}2 \times 10^{18} \text{ cm}^{-3}$  and a mobility of  $100 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$ . The free carrier concentration was lower than that obtained for best platelets elaborated through H.P.N.S.G. (Section 2.3.2). The CL spectrum exhibited a single peak at 265 nm. Brownish platelets synthesized through experiments without pressure regulation during the crystal growth presented not only this peak that was twice less intense but also another broad peak at 400–500 nm. This last one was not attributed but it was all the more intense as the crystals were colored or presented defaults. The good crystalline quality of the last crystals elaborated through the Na flux sodium crystal growth was then confirmed by these characterizations.

### 3.3. Optimizations of the Na flux process

The main disadvantage of the previous experiments was that a part of the gallium was used for the synthesis of gallium nitride in small crystals to the detriment of the larger platelets. A new BN vessel was then designed with an inner cone-shaped cavity that induced a curvature of the Na–Ga melt, in order to reduce the formation of the polycrystalline layer of GaN [53]. The authors also supposed that the impurities contained in the flux catalyzed its formation and proposed to use a flux with a higher purity [54]. In order to reduce the formation of the polycrystalline layer of GaN, experiments were carried out with a conic-shaped inner cavity of the BN vessel and eventually a high purity Na flux.

#### 3.3.1. Improvement of the vessel shape

**3.3.1.1. Experimental device.** The experiments in the BN vessel with a conic-shaped inner cavity were performed at  $750 \text{ }^\circ\text{C}$  and 5 MPa [53]. The formation of the polycrystalline GaN layer was thus reduced, no explanation being proposed in order to understand this phenomenon. Moreover, the conjugated effects between the wall angle and the melt curvature lowered the height of the wall that was wet by the liquid. Very few gallium nitride was thus formed on the wall of the vessel. Transparent and colorless crystals were grown in this vessel (in the polycrystalline layer): their size was greater than previously with platelets up to  $3 \text{ mm} \times 2.5 \text{ mm} \times 0.1 \text{ mm}$  ( $r_{Na} = 0.60$  and  $t = 360 \text{ h}$ ) and prisms about  $1 \text{ mm} \times 0.5 \text{ mm} \times 0.5 \text{ mm}$  ( $r_{Na} = 0.56$  and  $t = 450 \text{ h}$ ). For experiments with  $r_{Na} = 0.60$ , some gallium was remaining at the end ( $t = 360 \text{ h}$ ), while there was no gallium residue for  $r_{Na} = 0.56$  after 450 h. It should then be possible to elaborate larger platelets through an

increase of the duration for  $r_{\text{Na}} = 0.60$ . It was confirmed that the morphology changed from platelet to prism with a raise of the  $r_{\text{Na}}$  ratio. When its value was higher, nitrogen incorporation in the Na–Ga melt should be faster, as well as the formation of the  $\text{Na}_x(\text{GaN}_y)$  species. Yamane and co-workers [53] are still working on the influence on the  $r_{\text{Na}}$  ratio, this one playing a key rule on the crystals morphology during their growth.

**3.3.1.2. Properties of resulting crystals.** These crystals were characterized through photoluminescence and Raman scattering [55]. PL spectra usually presented a single band at 3.4 eV corresponding to the near band-edge emission, the yellow band not being observed (or very weakly). The largest platelets (3–4 mm) had a FWHM of the PL emission peak of 74 meV at room temperature and 2.2 meV at 1.7 K. It was decreasing down to 0.22 eV for smaller platelets. At room temperature, the prisms were characterized by a larger value (109 meV) and presented a broad band at 2.96 eV, revealing the presence of zinc as an impurity probably originating from the reagents. The free carriers concentration was evaluated by Raman scattering at about  $2\text{--}3 \times 10^{17} \text{ cm}^{-3}$  for 2–3 mm platelets and it decreased down to  $10^{16} \text{ cm}^{-3}$  for the smallest ones. These measurements confirmed the good crystalline quality of the platelets elaborated through this process [55].

The morphology and the polarity were studied through X-ray anomalous diffraction, for crystals obtained at 750 °C and 5 MPa [56]. As seen previously, the platelets exhibited a smooth (0 0 0  $\bar{1}$ ) face and a rough (0 0 0 1) one. The prisms were divided in two types: for pyramidal ones, the base was the (0 0 0 1) face while for the other ones, the large base was the (000 $\bar{1}$ ) face and the small one (at the top) the (0 0 0 1) face.

### 3.3.2. Purification of the Na flux

**3.3.2.1. Experimental device.** Using of a high purity Na (99.95%) flux, the formation of the polycrystalline layer on the surface of the Na–Ga melt during the experiments was stopped (750 °C, 5 MPa and 200 h for  $r_{\text{Na}} = 0.60$ ). With a lower purity flux (99%), a polycrystalline layer of GaN could be observed, thus confirming that impurity should originate its formation. In order to evaluate the influence of the impurity content, experiments were performed using as a 99.95% Na flux purified by distillation (775 °C, 5 MPa and 300 h for  $r_{\text{Na}} = 0.67$ ). The polycrystalline layer of GaN was not observed and platelet-shaped crystals (6 mm  $\times$  4 mm  $\times$  0.25 mm) were obtained in the bottom of the vessel. These platelets however certainly grew at the surface of the Na–Ga melt, held by the surface tension of the liquid. At 750 °C, Ga density was 5.67 and this of Na 0.77 while this of GaN was 6.1. When the content in Ga decreased, the surface tension was not high enough to keep up the platelet. The ratio N/Ga was smaller at the bottom of the vessel than in the surface of the melt where took place the dissociation of nitrogen molecules. The crystal growth was along the *c*-axis whereas it began perpendicularly to this axis (inducing the platelet shape). The platelet was thus convex, with a thickness of 0.25 mm [54].

The use of pyrolytic BN for the vessel led to platelet-shaped crystals, their size being about 10 mm [54]. Sintered BN that was used before for the vessel contained 0.5 wt% oxide additives, which led to impurities in the flux. The increasing size should not be only due to the high purity flux: pyrolytic BN presenting smoother wall than sintered one, the number of nucleation centers was reduced [54].

**3.3.2.2. Properties of resulting crystals elaborated in high purity Na flux.** The platelets were characterized by XRD: the FWHM of the (0 0 0 2) peak were 45 and 55 arcsec for the 6 and 10 mm sized crystal, respectively [54]. Those values were close (even smaller) to those of the crystals elaborated through H.P.N.S.G., for the same size.

### 3.4. Oriented crystal growth according to the Na flux process

#### 3.4.1. Oriented crystal growth induced by a substrate

In order to orientate GaN single crystals, Yano et al. [57] modified the experiences using  $\text{NaN}_3$  and Ga at 500–800 °C during 24 h, in stainless steel tubes, through the addition of a substrate. Most of the experiments using specific substrates [Si(1 1 1),  $\text{Al}_2\text{O}_3(0 0 0 1)$  or  $\text{SiC}(0 0 0 1)$ ] failed, except the one with  $\text{AlN}(0 0 0 1)$  film for which GaN crystallites were observed. In such a case their size depended on the experimental temperature (3  $\mu\text{m}$  at 600 °C, 26  $\mu\text{m}$  at 700 °C and 55  $\mu\text{m}$  at 800 °C). This increase of size with temperature was associated with a raise of the growth rate. XRD analysis showed that the *c*-axis of the wurtzite type GaN was normal to the  $\text{AlN}(0 0 0 1)$  film. The N/Ga atomic ratio of the resulting crystallites, evaluated by energy dispersive X-ray spectroscopy (EDXS), was also depending in the temperature; its value decreased from 1.22 at 800 °C to 0.98 at 700 °C and 0.80 at 600 °C. The deficiency of nitrogen in nitride gallium elaborated at low temperature could be due to the reduction of the nitrogen solubility in the Na–Ga melt. Cathodoluminescence (CL) spectra exhibited a peak corresponding to the near band-edge emission at about 3.4 eV, which FWHM value is reduced when experimental temperature decreased, from 212 to 109 meV at room temperature. Increasing temperature thus induced a raise in the crystalline quality of the elaborated crystals [57].

#### 3.4.2. Liquid phase epitaxy (LPE)

Liquid phase epitaxy was carried out by Kawamura et al. [58] using the Na flux method. The starting materials (Ga (1 g), Na (882 mg) and a 3  $\mu\text{m}$  (0 0 0 1) GaN substrate grown on a (0 0 0 1) sapphire one) were placed in a BN vessel (9 mm inner diameter and 50 mm height) and then heated to 800 °C at 5 MPa during 96 h. A GaN crystal (12 mm  $\times$  5 mm  $\times$  0.8 mm) was elaborated, larger than the used substrate. Its color changed from black in the early stages (indicating the presence for instance of many impurities or nitrogen vacancies) to transparent in the later ones. The MOCVD-GaN film exhibited many etch-pits after chemical etching, corresponding to a density of dislocation about  $1.3 \times 10^6 \text{ cm}^{-2}$ , on the contrary the LPE-GaN one had very few etch-pits, suggesting a low dislocation density. The PL spectra exhibited a peak (at 360 nm) 40 times stronger for the LPE-GaN film than for the MOCVD-GaN one. This reflected the increase of crystalline quality with the LPE method, the intensity being sensitive to the dislocation density [58].

A mixture of nitrogen and ammonia (40%) was also used instead of pure nitrogen, because previous studies [59] showed that adding  $\text{NH}_3$  in  $\text{N}_2$  during experiments using the Na flux method decreased the pressure threshold for GaN synthesis of about 2 MPa. A 10  $\mu\text{m}$  thick transparent GaN film was grown at only 0.5 MPa [58].

Kawamura et al. [60] tried to improve this process by swinging the pressure chamber during the LPE experiments. The BN vessel containing the starting materials was placed in the pressure chamber oscillating at a frequency of 1.5 times per second. This technique was thus called the flux film coated-liquid phase epitaxy (FFC-LPE) method. A growth rate of 4  $\mu\text{m h}^{-1}$  was obtained at 800 °C and 0.95 MPa using as a substrate a 15  $\mu\text{m}$  thick MOCVD-GaN film, leading in 4 h to a 15  $\mu\text{m}$  thick GaN film. This FFC-LPE film was quite smooth as it grew just below the gas–liquid interface. The color of the resulting film was light brown, indicating the presence of nitrogen vacancies probably due to the very low experimental pressure [60].

#### 3.4.3. Crystal growth from seeds

Aoki et al. [61] studied GaN crystal growth from seeds using the Na flux process. In order to optimize experimental conditions, the pressure and the temperature were explored, respectively, in the range 0.5–5 MPa and 750–850 °C, respectively. Three different cases were observed versus the values

of the pressure and the temperature. For the lowest pressures and temperatures, GaN seeds were decomposed because  $P$  and  $T$  were too small for stabilizing gallium nitride. For the highest pressures and temperatures,  $P$  and  $T$  were sufficiently high for inducing spontaneous nucleation of GaN without any crystallographic relation with the seeds. This  $P$ - $T$  field was the one explored previously for the Na flux crystal growth experiments. In an intermediate  $P$ - $T$  domain, gallium nitride nucleation could be obtained on the seeds.

The used GaN crystals as seeds were elaborated in previous mentioned experiments, (their length and thickness being 1–3 and 0.025–0.2 mm respectively) [52,53]. At 850 °C and 2 MPa it was possible to grow GaN crystals up to 3 mm × 1.5 mm × 1 mm in 200 h. Their X-ray Laue photograph, with the beam parallel to the  $c$ -axis of a as-grown crystal, confirmed that a single crystal was developed on the seeds. The as grown crystals exhibited a dark color, similar to this obtained in Ga rich conditions, which should be due to a nitrogen deficiency. This result could originate from the low nitrogen pressure used during these experiments. The growth rate along  $c$  ( $1\text{--}4 \mu\text{m h}^{-1}$ ) was higher than that along  $a$  ( $1 \mu\text{m h}^{-1}$ ), the experimental  $P$ - $T$  conditions being very close to those for which prisms were elaborated [61].

### 3.5. Dissolution and recrystallization of gallium nitride in molten Na

Recently, Aoki et al. [62] further studied the Na flux process, through the dissolution of GaN in molten Na and its recrystallization.

#### 3.5.1. Dissolution of GaN in molten Na

For the investigation of the dissolution of GaN in molten Na, sodium and GaN polycrystalline fragments (elaborated by the Na flux method) were introduced in a BN vessel under inert conditions. This one was then placed in the high pressure reactor where the experiments were carried out, (the explored temperature and nitrogen pressure being 650–800 °C and 3–5 MPa). The mass dissolution of GaN (expressed in mg/g of sodium) was evaluated through the mass loss of GaN and through the mass of metallic gallium obtained after removing the sodium, the results obtained by both ways being consistent. The Ga dissolution increased with the temperature: from about 2 mg/g<sub>Na</sub> at 650 °C to 37 mg/g<sub>Na</sub> at 5 MPa or from 1 mg/g<sub>Na</sub> to 27 mg/g<sub>Na</sub> at 3 MPa (for 100 h duration). The increase of the nitrogen pressure induced the decrease of the GaN mass dissolution. Aoki et al. [62] proposed the hypothesis of the formation of  $\text{Na}_x[\text{GaN}_y]$  species in the Na melt to explain the raise of the nitrogen solubility compare to this in pure Ga melt (see Section 3.2.2).

The addition of a small amount of  $\text{Li}_3\text{N}$  (3.5 wt% Na) led to an increase of the mass dissolution of GaN, up to 40% at 800 °C. The author assumed that species including Li and Ga were formed when lithium nitride dissolved into Na melt ( $\text{Li}_3\text{N}$  playing the role of mineralizer in the Na flux method).

#### 3.5.2. Recrystallization of GaN in molten sodium

The first recrystallization experiments were carried out in the apparatus described in the previous part using Na (1 g), GaN powder (15–20 mg) as a nutrient and  $\text{Li}_3\text{N}$  (3.5 mg) in some cases. The GaN powder was constituted of <30  $\mu\text{m}$  crystallites issued from crushed GaN crystals elaborated by the Na flux process. After reaching experimental conditions (800 °C and 5 MPa during 50 h), the sample was slowly cooled ( $1 \text{ }^\circ\text{C h}^{-1}$ ) down to 700°, the heating being then stopped. Brown hexagonal crystals up to 100  $\mu\text{m}$  were elaborated without  $\text{Li}_3\text{N}$  as an additive [62]. The crystals obtained with lithium nitride (on the vessel wall) were transparent and colorless platelets which size could be up to 300  $\mu\text{m}$ , thanks to the improvement of GaN mass dissolution in Na in presence of  $\text{Li}_3\text{N}$ . The sites where such crystals were observed suggested that the growth began after the total dissolution of the nutrient. Aoki

et al. expected that crystal growth of larger crystals should be realized using in addition a thermal gradient [62].

### 3.6. Development of other fluxes for GaN crystal growth

#### 3.6.1. Crystal growth using a potassium flux

Yamane et al. [63] observed that gallium nitride synthesis using a K flux led to blende-type GaN (cubic). Up to 30  $\mu\text{m}$  black or transparent crystals were obtained with the following experimental conditions: 750  $^{\circ}\text{C}$ , 7 MPa, 100 h,  $r_{\text{K}}$  value of 0.4 ( $r_{\text{K}} = n_{\text{K}}/[n_{\text{K}} + n_{\text{Ga}}]$ ). The squared facet as well as the four-fold or three-fold axis observed by SEM reflected the symmetry of the blende structure. The authors did not propose any hypothesis in order to explain why potassium flux stabilized rather blende-type GaN than wurtzite-type structure [63]. XRD characterizations on a 40  $\mu\text{m}$   $\times$  30  $\mu\text{m}$   $\times$  30  $\mu\text{m}$  GaN prism led to a lattice parameter  $a = 4.5062 \text{ \AA}$ , in the range of the values obtained for cubic GaN films (4.49–4.53  $\text{\AA}$ ). CL spectra evidenced a peak at 3.2 eV corresponding to the near band-edge emission and a broad one at 2.4–2.8 eV suggesting the presence of deep levels originating in defaults or impurities. The value of the band-gap was then 3.2 eV (0.2 eV below the value of the wurtzite-type GaN one) that was consistent with the measurements realized on films [63].

Yamane et al. [64] also reported the synthesis of cubic GaN with Na flux, the experimental condition being: 570  $^{\circ}\text{C}$ , 200 h,  $r_{\text{Na}}$  ratio of 0.75. The temperature was chosen 10  $^{\circ}\text{C}$  below the melting temperature of the  $\text{Ga}_{39}\text{Na}_{22}$  intermetallic compound. The GaN crystals obtained at the bottom of the vessel exhibited a morphology corresponding to cubic structure (truncated slab). Powder X-ray patterns presented a mixture of blende-type ( $a = 4.5019(1) \text{ \AA}$ ) and wurtzite-type ( $a = 3.1887(1) \text{ \AA}$  and  $c = 5.1833(4) \text{ \AA}$ ) gallium nitride. The polycrystalline layer and the crystals on the surface of the vessel wall were wurtzite-type GaN [64].

#### 3.6.2. Crystal growth using a lithium flux

Song et al. [65] recently elaborated transparent and colorless GaN crystallites using a Li flux. A tungsten sealed tube containing a mixture of Ga and  $\text{Li}_3\text{N}$  was very slowly cooled (2–3  $^{\circ}\text{C day}^{-1}$ ) during 120–180 h. The initial temperature had to be in the range 740–800  $^{\circ}\text{C}$ ,  $\text{Li}_3\text{N}$  corroding the tube above 800  $^{\circ}\text{C}$  and no GaN being formed below 740  $^{\circ}\text{C}$ . The Ga/ $\text{Li}_3\text{N}$  molar ratio had to be between 1 and 4 because an excess of lithium led to the synthesis of  $\text{Li}_3\text{GaN}_2$  while this of gallium allowed the exclusive formation of GaN. The crystallites exhibited more or less regular (hexagonal) morphologies, their thickness being between 20 and 300  $\mu\text{m}$ . Their XRD powder pattern was characteristic of a wurtzite-type structure with  $a = 3.1903(3) \text{ \AA}$  and  $c = 5.1864(6) \text{ \AA}$ . The (1 0 1) peak FWHM for single crystal XRD was about 10–30 arcsec which revealed a good crystalline quality. Song et al. proposed a crystal growth mechanism in two steps [65]. The first one should be the formation of  $\text{Li}_3\text{GaN}_2$  and of the Li flux ( $\text{Ga} + 2\text{Li}_3\text{N} \rightarrow 3\text{Li} + \text{Li}_3\text{GaN}_2$ ), the second step leading to the synthesis of GaN through the decomposition of  $\text{Li}_3\text{GaN}_2$  ( $\text{Li}_3\text{GaN}_2 \rightarrow 3\text{Li} + 2\text{GaN}$ ). The authors proposed that a Li–N–Ga liquid phase was formed within which the nucleation and the crystal growth of GaN took place [65].

#### 3.6.3. Crystal growth using mixed fluxes (Na, Ca, Li, ...)

Kawamura et al. [66] studied GaN synthesis using a mixed Ca–Na flux. The reagents (Ga (1 g), Na and Ca, according to a molar Ga/flux ratio of 0.27) were introduced in a BN vessel and then placed into a stainless steel tube. This one was then connected to the pressure and heating apparatus. The experimental temperature and pressure were 800  $^{\circ}\text{C}$  and 3 MPa, respectively, for duration of 96 h. The yield of reaction increased with Ca content from 1.4% without Ca, up to 14% for Ca amount of 10 mol% and above 30 mol% the yield was zero. Moreover, the nitrogen pressure threshold was

reduced to about 1 MPa by using a 10 mol% Ca flux instead of a pure Na flux. The elaborated crystallites were quite small (up to 100  $\mu\text{m}$ ) but were transparent when growing near the gas–liquid interface, due to their lower nitrogen vacancies concentration (Ca promoting nitrogen incorporation in the melt). No crystal growth mechanism was described [66]. The Na–Ca flux was used for the LPE method (see Section 3.4.2) by Kawamura et al. [67] and large crystals were elaborated at 800 °C during 96 h, the thickness being from 150  $\mu\text{m}$  at 1 MPa to 600  $\mu\text{m}$  at 5 MPa. They were almost totally transparent, certainly thanks to the larger nitrogen solubility in the melt.

The Li–Na flux system was also investigated by Morishita et al. [68] exactly in the same conditions than these used for the Na–Ca flux experiments, the pressure being 1.5 MPa. The yield of the reaction increased with Li content up to 84% for a Li amount of 70 mol%, to 0 for pure Na or pure Li. The crystallites morphology changed from prismatic to platelets with Li ratio increasing. Moreover, their sizes were higher than these with Na–Ca flux, reaching 800  $\mu\text{m}$ . Finally, their color varied from black to transparent when the content in lithium was raising, underlining the decreasing of N vacancies concentration probably due to an increased amount of nitrogen in solution [68].

#### 3.6.4. Growth of GaN crystals from molten solution

GaN single crystals have been grown at moderate temperature (close to 800 °C) and pressure (25 bar of  $\text{N}_2$ ) using a molten solvent with the composition  $\text{LiF–BaF}_2\text{–Li}_3\text{N}$  with an approximate ratio 1/1/1 by Feigelson and Henry [69]. Wurtzite-type rod-shaped GaN single crystals (0.5 mm length) were been observed, sintered GaN, used as nutrient, being dissolved into the solvent.

## 4. Ammonothermal crystal growth

### 4.1. The ammonothermal crystal growth

In the middle of the 1990s, Dwilinski et al. [70,71] studied the ammonothermal synthesis of gallium nitride, which was then called the Ammono method. GaN synthesis was realized in supercritical ammonia, from metallic gallium, at a temperature of 500 °C and a pressure in the range 400–500 MPa. A mineralizer was added, such as lithium or potassium amide (the reaction of ammonia with metallic gallium being limited on the surface of the Ga particles). A molar  $\text{MNH}_2\text{:NH}_3$  (M = Li, K) ratio of 1:10 led to micrometric faceted crystallites in 72 h with  $\text{LiNH}_2$  as a mineralizer [70]. Their crystalline quality was highly depending on the content in added amide. For a lower molar ratio (for instance 1:240), only the surrounding of the Ga grains was converted in GaN, leading to irregular gray particles. Needles with a maximum size of 25  $\mu\text{m}$  were prepared with  $\text{KNH}_2$  [71].

Crystallites elaborated with  $\text{LiNH}_2$  as a mineralizer were characterized through X-ray diffraction, electronic paramagnetic resonance (EPR) and photoluminescence [70,72,73]. The gallium nitride was solely wurtzite-type [ $a = 3.1885(2)\text{\AA}$  and  $c = 5.1842(4)\text{\AA}$ ] [70]. The PL spectra exhibited a strong yellow band – associated with vacancies – with a broad band at 1.5–2.9 eV. This yellow band was much diminished for crystallites that were prepared with rare earth (their nature not being specified by the authors) in order to trap oxygen atoms. On the other hand, the very thin peak corresponding to the near band-edge emission was observed with a FWHM of 1 meV [73]. This underlined the efficiency of the RE for trapping oxygen, Ga vacancies being certainly associated to impurities such as oxygen. The free electron concentration was evaluated through EPR, by comparison with a p-doped Si standard sample, to  $5 \times 10^{15} \text{ cm}^{-3}$  for the crystallites elaborated with RE. This value was the lowest ever reported and was not confirmed by later measurements [72].

The authors did not publish more recent results about the synthesis of GaN crystals. However, they showed that the dissolution of H.P.N.S.G. GaN crystals in supercritical ammonia was feasible at 550 °C and 500 MPa in the presence of mineralizers [70].

In parallel GaN crystal growth was initiated through a solvothermal process using  $\text{NaN}_3$  and gallium as precursors and ammonia as solvent [74]. In such a process  $\text{N}_3^-$  acted as nitriding agent and N as Na flux leading to the growth of GaN crystallites.

After different works involving GaN crystal growth with a maximum size of 10 mm by heating Na–Ga melts at 750–800 °C and 5 MPa of  $\text{N}_2$  pressure during 200–300 h. Aoki et al. proposed an optimized crystal growth method using addition of  $\text{Li}_3\text{N}$  in the flux and a temperature gradient method [75].

#### 4.2. Improvements of the ammonothermal crystal growth

At the end of the 1990s, Kolis et al. [14] performed the crystal growth of gallium nitride in supercritical ammonia thanks to mineralizers such as sodium or potassium amide. They adapted the hydrothermal crystal growth of  $\alpha$ -quartz (or other various oxides) using ammonia as a solvent and gallium nitride as a nutrient. Kolis et al. [14] supposed that it should be possible to dissolve – even very slightly by means of a mineralizer – GaN in  $\text{NH}_3$  (GaN being insoluble in pure ammonia). The supposed mechanism of GaN crystal growth would be the following:  $\text{GaN} + \text{NH}_2^- + 2\text{NH}_3 \rightarrow [\text{Ga}(\text{NH}_2)_4]^- \rightarrow \text{GaN} + \text{NH}_2^- + 2\text{NH}_3$ .  $\Delta T$  played a role on the formation/dissociation of the complex  $[\text{Ga}(\text{NH}_2)_4]^-$ . The rule of the various mineralizers is described in the next parts.

More recently Chen et al. [76] modeled different ammonothermal systems able to give bulk single crystals of GaN and AlN using fluid dynamics, thermodynamics and heat transfer models.

The transposition of the hydrothermal crystal growth of  $\alpha$ -quartz was also studied recently by Denis et al. [77] which performed its first step: the solvothermal transport of gallium and nitrogen with  $\text{Li}_3\text{GaN}_2$  as a nutrient and ammonia as a solvent. The nitride  $\text{Li}_3\text{GaN}_2$  was used in order to improve the dissolution step due to its higher ionicity than gallium nitride. XPS analysis showed the feasibility for the transport and the formation of the GaN deposit on silicon substrates at moderate pressures and temperatures ( $\sim 150$  °C and 150–200 MPa) via a three-steps mechanism: (i) solubilization of  $\text{Li}_3\text{GaN}_2$  and formation of the “ $\text{GaN}_2^{3-}$ ” species ( $\text{Li}_3\text{GaN}_2 \rightarrow \text{GaN}_2^{3-} + 3\text{Li}^+$ ), (ii) transport of this  $\text{GaN}_2^{3-}$  species to the substrate and (iii) then precipitation of GaN on this one ( $\text{GaN}_2^{3-} \rightarrow \text{GaN} + \text{N}^{3-}$ ) [77].

Phase diagram of the system Li–Ga–N was constructed and assessed using the CALPHAD method [78]. This thermodynamical approach suggests that GaN crystal could be grown from the Ga rich Li–Ga–N ternary solution using moderated  $\text{N}_2$  pressure and temperature. Growth of GaN single crystal have been claimed at 800 °C under normal nitrogen pressure (105 Pa).

Ammonothermal growth of GaN via fluid transport in supercritical ammonia was very recently described by Hashimoto et al. [79]. Such a research work underlines that the solubility of GaN would have a negative temperature dependence. Consequently the GaN nutrient was placed in the lower temperature zone and through weight gain GaN grows.

##### 4.2.1. Use of alkaline amide as mineralizers

In order to evidence the role of mineralizers, Kolis et al. [14] performed experiments with amorphous GaN, as nutrient prepared through the treatment of gallium chloride with an ammonia flux. The nutrient (125 mg) and the mineralizer (250 mg) were introduced in a high pressure vessel made of Rene 41 alloy ( $V = 12.5$  ml). This one was then filled with ammonia by a low temperature

distillation–recondensation process. The experimental conditions were optimal at 380 °C and 270 MPa (corresponding to a filling rate of 80%) [14].

Up to 0.4 mm crystals were elaborated in 72 h with  $\text{NaNH}_2$  as a mineralizer. XRD (on powder) confirmed the wurtzite-type structure for the resulting GaN. The experimental temperature was chosen below 450 °C in order to remain in the Haber equilibrium ( $\text{NH}_3$  molecules decompose into nitrogen and hydrogen above this temperature, pressure avoiding it below [14]).

Similarly experiments were realized with commercial crystalline GaN powder but they did not lead to GaN recrystallization. Chemical analysis showed that the amorphous GaN prepared by the authors was containing chlorine traces. As potassium or sodium amide were not sufficient to help gallium nitride solubilization, chloride was added to improve this step.

Experiments were then carried out adding KCl to  $\text{KNH}_2$  and led to the elaboration of GaN crystals from commercial GaN powder [14]. In the present state the role of chloride or chloride anion is not exactly understood.

#### 4.2.2. Use of alkaline amide and halogenide as mineralizers

The nature of the mineralizer ( $\text{MNH}_2$ ,  $\text{M} = \text{Na}, \text{K}$ ) and that of the co-mineralizer ( $\text{MX}$ ,  $\text{M} = \text{Li}, \text{Na}, \text{K}$  and  $\text{X} = \text{Cl}$ ) was recently studied [80]. Its choice was crucial, the mixture ( $\text{KNH}_2 + \text{KI}$ ) leading to the best results (their solubility being the highest for the alkaline metal amide and halogenide). Moreover, the  $\text{KNH}_2/\text{Ga}$  molar ratio must be controlled: (i) above 6:1, there was no crystallization and (ii) below 3:1 the growth rate was too small. The largest crystals were elaborated in the following experimental conditions:  $T = 400$  °C,  $P = 240$  MPa (corresponding to a  $\text{NH}_3$  filling rate of 80%),  $t = 7$  days and  $\text{KNH}_2:\text{KI}:\text{Ga} = 60:1:20$  (molar ratios). The resulting crystals were transparent platelets or prismatic needles, up to  $0.5 \text{ mm} \times 0.2 \text{ mm} \times 0.1 \text{ mm}$ . They were located within the GaN powder that did not react. Their XRD characterization confirmed the wurtzite-type structure [ $a = 3.182(5)\text{Å}$  and  $c = 5.178(3)\text{Å}$ ]. As for alkaline amide the role of the halogenide was not yet cleared up, Kolis et al. presuming that it should act in the nutrient attack in order to form an initial halogenide complex. The transport should then occur thanks to the  $\text{NH}_2^-$  anion, as “gallium–imide–amide” or “gallium–nitride–amide” complexes [80].

#### 4.3. Optimizations of the ammonothermal crystal growth

Very recently, experiments similar to the previous ones were performed by Kolis and co-workers [15] using potassium azide as a mineralizer (this one being more efficient than the mixture of alkaline amide and halogenide for solubilizing the nutrient). Prismatic needles and platelets ( $<1$  mm) were elaborated at 500 °C during 240 h, using GaN powder and/or crystals as a nutrient, the  $\text{KN}_3$  concentration being 1.3 or  $1.6 \text{ mol l}^{-1}$ . For high  $\text{KN}_3$  concentration, only platelets were obtained whereas low one led to a mixture of prisms and platelets. By analogy with H.P.N.S.G. mechanism, prismatic growth should occur in a domain out of equilibrium experimental conditions at low concentrations. When the  $\text{KN}_3$  concentration increased, the transport should be improved and the platelets morphology should be favored [15].

The obtained crystals were characterized through XRD and transmission X-ray topography. They all exhibited the wurtzite-type structure and the X-ray diffraction FWHM were in the range 17–266 and 7–64 arcmin (1 arcmin = 60 arcsec) for the platelets and the prisms, respectively. The transmission X-ray Laue photographs showed that needles grew along the  $c$ -axis and platelets perpendicularly to the (0 0 0 1) plane. Prisms exhibited quite well defined spots whereas those of the platelets presented various amount of streaking revealing a high mosaicity (20–300 arcmin against  $\sim 10$  arcmin for the prisms). The dislocation density of the crystals (platelets) presenting the best crystalline quality,

was evaluated using X-ray topography. Its value was at least equal to  $10^6 \text{ cm}^{-3}$  which was consistent with the FWHM value for XRD peaks. These results were far from those of the GaN crystals obtained by H.P.N.S.G. or Na flux methods (Sections 2.3.2 and 3.2.3), corresponding to a lower crystalline quality of these crystals [15].

#### 4.4. Synthesis and recrystallization of gallium nitride in acido-basic media

##### 4.4.1. Ammonothermal synthesis of GaN in acidic medium

At the end of the 1990s, Purdy [81] studied the ammonothermal synthesis of gallium nitride from metallic gallium with ammonium halogenide ( $\text{NH}_4\text{X}$ , X = Cl, Br, I) ( $\text{NH}_4^+$  being the acidic form of  $\text{NH}_3$ ) and claimed that blende-type (cubic) GaN was elaborated. Gallium and  $\text{NH}_4\text{X}$  were introduced in a quartz tube that was filled with ammonia before sealing. The tube was then placed into a high pressure vessel full of water (acting as a pressure transmitting medium), the initial pressure being adjusted to 70 MPa. During the heating, there was a thermal gradient about  $10 \text{ }^\circ\text{C cm}^{-1}$  in the quartz tube (the coldest part being the top of the tube). At the end of the experiment, the reaction products were washed with alcohol and acetone. The obtained powder was characterized by XRD, the hexagonal and cubic phases amounts being evaluated by comparison between their respective diffraction peak intensities and those of an equimolar mixture of these two phases. The following experimental parameters were investigated: the temperature, the  $\text{NH}_3$  filling rate of the tube quartz (inducing the pressure), the halogenide nature in  $\text{NH}_4\text{X}$  and its concentration.

The analyses of the results led to the following conclusions [82]:

- (i) At temperatures below  $\sim 440 \text{ }^\circ\text{C}$ , the whole synthesized GaN was at the bottom of the tube as an off-white to yellowish brown fine powder.
- (ii) At lower temperature ( $\sim 300 \text{ }^\circ\text{C}$ ), the obtained X-ray diffractograms mainly contained peaks characteristic of the blende-type structure, those of the wurtzite-type one being broad (the low temperatures seemed to favor the blende-type gallium nitride).
- (iii) At temperature above  $\sim 440 \text{ }^\circ\text{C}$ , GaN microcrystals were formed at the top of the tube wall (thus, a solvothermal transport of the product seemed to occur, with growth of crystalline material in the upper (colder) part of the tube).
- (iv) When cubic and hexagonal phases coexisted, the first one was always in the coldest part (globally, the deposited GaN amount raised with decreasing the vessel filling or with increasing  $\text{NH}_4\text{X}$  content).
- (v) Bromide ions favored rather the crystal growth rate than iodide ones, but led to wurtzite-type needle like gallium nitride.

The ammonothermal synthesis of blende-type GaN seemed to result from a complicated process kinetically controlled. The wurtzite structure was thermodynamically favored but the synthesis of the blende-type structure was possible through a process involving a low activation barrier [82].

##### 4.4.2. Ammonothermal recrystallization of GaN in so called "acidic medium"

Recrystallization experiments in supercritical ammonia from wurtzite-type (hexagonal) gallium nitride were realized very recently by Purdy [82], leading to the growth of blende-type (cubic) GaN crystals. The experimental procedure was nearly the same as previously, the pressure being higher, in the range 210–280 MPa. The thermal gradient was still about  $10 \text{ }^\circ\text{C cm}^{-1}$ , inducing a temperature difference between the bottom and the top of the tube about 140–180  $^\circ\text{C}$ . The following analyses could be drawn up from the various realized experiments [82]:

- (i) Whatever the used halogenide, hexagonal gallium nitride was dissolved in the hot part of the tube and GaN crystals were deposited in the cold part (at the top) of the tube.
- (ii) Concerning the resulting GaN structure although most of the deposited nitride was cubic (>80%), hexagonal GaN was always formed (the wurtzite-type phase should be the first one that grew on the wall tube, probably because of the presence of lost seeds from the nutrient).
- (iii) The experimental conditions seemed to control the morphology of the elaborated micrometric crystals: cone-shaped crystals, small cluster of needles, globular deposit or triangular prismatic needles. Especially, the last ones were obtained with a low  $\text{NH}_4\text{Cl}$  concentration (0.28 mol%) and a high LiCl one (2.0 mol%), for an ammonia tube filling of 55%.

A needle-shaped crystal (0.16 mm in length, 0.2 and 0.005 mm in diameter at the base and the apex), respectively, was characterized of XRD. Its structure was blende-type with  $a = 4.512(5)\text{\AA}$ . The base and the apex corresponded to the  $(\bar{1}1\bar{1})$  and  $(1\bar{1}1)$  faces, and the three faces in the length to the  $(011)$ ,  $(\bar{1}\bar{1}0)$  and  $(10\bar{1})$  ones, this orientations being confirmed for various needles [82].

The GaN chemical transport rate seemed not to be linear with the  $\text{NH}_4\text{X}$  concentration, but presented a maximum. This phenomenon was similar to this observed for hydrothermal crystal growth of  $\alpha$ -quartz. In both cases when the mineralizer concentration was too high, there was no transport at all. GaN dissolution indeed should imply the formation of alkaline halogenides, and the deposition, the ammonolysis and the condensation of these halogenides in GaN and  $\text{NH}_4\text{X}$ . According to Le Chatelier's principle, an excessive amount of  $\text{NH}_4\text{X}$  should weaken the ammonolysis. Purdy proposed the following reactional mechanism: (i) in the hot zone, the solubilization of GaN:  $(\text{GaN})_n + z\text{NH}_4\text{X} \rightarrow \text{Ga}_n\text{N}_w(\text{NH})_x(\text{NH}_2)_y\text{X}_z$ , with an infinite number of possibility for the intermediary species (these ones being different for the hexagonal and the cubic phases), (ii) in the cold zone, the ammonolysis:  $\text{Ga-X} + 2\text{NH}_3 \rightarrow \text{Ga-NH}_2 + \text{NH}_4\text{X}$  [82].

The control of the synthesis conditions and the use of seeds should allow Purdy to grow blende-type GaN crystals. A larger platinum tube was also envisaged [81]. Moreover, the synthesis of GaN was realized from gallium iodide (instead of metallic gallium) at 300 °C and 515 °C [74]. The ammonolysis of  $\text{GaI}_2$  led only to the hexagonal phase whereas the one of  $\text{GaI}_3$  to cubic GaN. The addition of CuI or LiI led to the pure cubic phase but the crystal growth was not possible (only a powder constituted of micrometric crystallites was deposited in the cold part of the sealed quartz tube) [83].

#### 4.4.3. Ammonothermal recrystallization of GaN in a basic medium

Ammonothermal conditions for growing GaN bulk crystals using GaN as nutrient were developed by Callahan et al. [84]. Experiments were performed in ammono-basic solutions (ammonia with addition of molaramide) in high nickel content autoclaves in a temperature range 400–600 °C and a pressure range 100–300 MPa for up to 3 weeks – single crystal clusters on the order of 500  $\mu\text{m}$ –1 mm long were obtained.

#### 4.5. Ammonothermal recrystallization of GaN from Ga as nutrient

Recently the growth of GaN via fluid transport in supercritical ammonia was evaluated by Hashimoto et al. [79]. Metallic gallium was used as nutrient in the low temperature zone of a reaction vessel, GaN single crystal seeds being placed in the high temperature zone. Spontaneously nucleated precipitates on the GaN seeds were observed, the maximum size of such precipitates being 10  $\mu\text{m}$ .

## 5. Growth of doped GaN single crystals

The potentialities of new developments in field of spintronics for GaN doped systems have recently concentrated interest on the growth of doped GaN bulk single crystals [85].

Besides H.P.N.S.G. process performed for the elaboration of Mg or Be doped crystals and reported in Section 2.4, other routes were investigated. Szyszko et al. [86] reported the synthesis of  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  single crystal ( $x \approx 0.05$ ) using a flow reactor system by the reaction of a Ga/Mn alloy with  $\text{NH}_3$ . A crystal ( $3.0 \text{ mm} \times 1.5 \text{ mm} \times 0.4 \text{ mm}$ ) was obtained in the temperature range (1000–1050 °C) with a  $\text{NH}_3$  flow rate close to  $80\text{--}100 \text{ h}^{-1}$  during 5–8 h.

More recently the potentialities to prepare  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  single crystal were investigated by Geiser et al. [87]. Gallium nitride single crystals substituted by Al (27%) were obtained in severe experimental conditions ( $T = 1850 \text{ °C}$ ,  $P = 3.5 \text{ GPa}$ , duration 3 days) using solid nitride precursors.

In the near future the growth of doped GaN single crystals will probably be developed through the different crystal growth processes.

## 6. Conclusions

### 6.1. Summary of the characteristics of the various developed processes

The previously reviewed crystal growth processes all present disadvantages and advantages that will be analyzed thanks to the following tables summarizing the experimental conditions and the structural and electric properties of the resulting crystals (Tables 1 and 2).

### 6.2. Advantages of the various analyzed processes

#### 6.2.1. Advantages linked to the development of the crystal growth processes

All these processes present very few advantages from an experimental standpoint. They require conditions (pressure and temperature) quite severe and/or the use of toxic and/or reactive compounds.

The following advantages can however be brought out: (i) the Na flux method is realized at temperature and pressure rather moderate, thus it should not be absolutely impossible to use it industrially and (ii) the ammonothermal method can be performed at a very low temperature and an accessible pressure (this one is in the same range than the one involved in the  $\alpha$ -quartz crystal growth, a process developed industrially [88]).

#### 6.2.2. Advantages linked to the elaborated crystals

High quality crystals are elaborated through the H.P.N.S.G. process: (i) the crystalline quality is very high with a low dislocation density and a very small FWHM of the X-ray diffraction peaks and (ii) the free carrier concentration is considerably lowered with p-type doping with magnesium, improving their crystallinity thanks to a decrease of the dislocation concentration.

Table 1  
Experimental conditions of the processes H.P.N.S.G, Na flux and ammonothermal

Method (authors)	Pressure	Temperature (°C)
H.P.N.S.G. (Porowski et al. [10,12,16–41])	1–2 GPa ( $\text{N}_2$ )	1400–1500
Na flux (Yamane et al. [13,48–64])	5–10 MPa ( $\text{N}_2$ )	700–800
Ammonothermal (Kolis et al. [14,15])	200–300 MPa ( $\text{NH}_3$ )	400–500

Table 2

Structural and electrical properties of the crystals elaborated through the H.P.N.S.G, Na flux and ammonothermal processes

Method (authors)	Maximum size of the crystals	FWMH of X-ray diffraction peaks	Defaults
H.P.N.S.G. (Porowski et al. [10,12,16-41])			
Non-doped	12 mm × 10 mm × 0.1 mm	20–30 arcsec for <3 mm crystals 40–50 arcsec for >4 mm crystals	$\rho_{\text{dislocation}} < 2 \times 10^2 \text{ cm}^{-2}$ $[V_{\text{Ga}}] = 10^{18} \text{ cm}^{-3}$
P-doped	Similar to non-doped crystals	18–25 arcsec	$\rho_{\text{dislocation}} \sim 10\text{--}10^2 \text{ cm}^{-2}$ $[V_{\text{Ga}}] \sim 0 \text{ cm}^{-3}$
Na flux (Yamane et al. [13,48-64])	6 mm × 4 mm × 0.25 mm (10 mm × 4 mm × 0.1 mm)	45 arcsec (55 arcsec)	–
Ammonothermal (Kolisetal. [14,15])	<1 mm	17–200 arcmin	$\rho_{\text{dislocation}} > 10^6 \text{ cm}^{-2}$

Methods (authors)	Oxygen concentration	Free carrier concentration	Mobility
H.P.N.S.G. (Porowski et al. [10,12,16-41])			
Non-doped	$10^{18}\text{--}10^{19} \text{ cm}^{-3}$	$5 \times 10^{19} \text{ cm}^{-3\text{a}}$	$60 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$
P-doped	–	Resistivity of $10^4\text{--}10^6 \Omega \text{ cm}$ or very weak p-type conductivity	
Na flux (Yamane et al. [13,48-64])	–	$10^{16}\text{--}10^{18} \text{ cm}^{-3\text{a}}$	$10\text{--}100 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$
Ammonothermal (Kolis et al. [14,15])	No characterizations has been published yet		

 $\rho_{\text{dislocation}}$  = dislocation density;  $[V_{\text{Ga}}]$  = concentration of Ga vacancies.<sup>a</sup> Non-intentional n-type doping with oxygen.

Concerning the Na flux method, there is no data on the dislocation density or on the density of Ga vacancies for realized the crystals. The FWHM of the XRD peak is very low, involving probably a good crystalline quality. Moreover, crystals with a free electron concentration twice smaller than the one obtained by the H.P.N.S.G. were elaborated through the Na flux process. These results suggest that the oxygen concentration in those crystals is smaller than this of the H.P.N.S.G. crystals (sodium probably trapping oxygen before its integration in the gallium nitride lattice).

### 6.3. Disadvantages of the various described processes

#### 6.3.1. Disadvantages linked to the development of the crystal growth processes

First of all, these methods share the disadvantage that the atmospheres in which the experiments are performed require a severe control of oxygen contamination because the synthesis of gallium oxide is a predominant problem. The involved constraints are the use of a glove box in inert atmosphere during the preparation and the drastic elimination of water or oxygen traces in the precursors and the experimental devices before the crystal growth.

Furthermore, too severe experimental conditions (pressure and temperature) limit the development of a process on a large scale, as for instance the H.P.N.S.G. one. The pressure about 1–2 GPa associated with the temperature of 1500 °C can be reached only with a very limited and expensive apparatus (any increase of size, in order to elaborate larger crystals, required substantial efforts for the control of the experimental conditions, the reliability of the devices and consequently their price).

At the experimental level, the use of some chemical compounds can hinder the transfer of a process to the industrial scale. For instance, the sodium that is used in the flux method is very reactive and must be handled in controlled conditions. Moreover, it has to be highly pure or else the size and the crystalline quality of the elaborated crystals are largely diminished. The ammonia used for the ammonothermal method is very corrosive and its handling is much more sensitive than the one of nitrogen.

#### 6.3.2. Disadvantages linked to the elaborated crystals

Firstly, the crystals elaborated through the various processes described previously are too small, the greatest dimension of the obtained hexagonal platelets being 12 mm, that correspond to an area less than 200 mm<sup>2</sup>. The area of the substrates that is usually developed industrially is at least 10 times larger (2 inches in diameter).

Furthermore, these methods lead to non-intentionally n-doped crystals because of a quite large concentration in oxygen: on the one hand, the so-induced Ga vacancies concentration is also high and on the other hand the electron mobility is limited (their mobility being inversely proportional to the free carrier concentration).

Finally, the published results for the ammonothermal method are quite restricted but the crystalline quality of the obtained crystals seems to be rather poor, the FWHM of the XRD peaks being very high. Moreover, the maximal size of these crystals is 3 mm. All this should probably be improved with a seeded crystal growth, associated with a control of the experimental parameters, this method being at the first stage of its development.

### 6.4. Gallium nitride wafers elaboration

Finally, the realization of few centimeters in diameter GaN wafers by the slicing of bulk polycrystalline gallium nitride (realized through various processes) had to be noticed because they should be used for the fabrication of optoelectric or electronic devices.

- (i) Sukhovev et al. [89,90] elaborated GaN ingots for TDI, Inc. through a low pressure–low temperature crystallization from liquid gallium on a GaN buffer. The pressure and the temperature were, respectively, 0.2 MPa and 800–1000 °C, leading to growth rate about 1–2 mm h<sup>-1</sup>. These ingots were 2.5 inches in diameter and 12 mm in length and the resulting wafer presented monocrystalline zones (5–7 mm) [91].
- (ii) Vaudo et al. [92–94] realized GaN boules for ATMI, Inc. by Hybrid Vapor Phase Epitaxy (from chloride gallium at 900–1100 °C) using HVPE-GaN layer as a substrate. The growth rates were lower in the range 0.05–2 mm h<sup>-1</sup>. Their dimensions were 30 mm in diameter and 5 mm in thickness. The value of the FWHM of the (0 0 0 4) peak was 38 arsec [93] and the dislocation density was rather low (10<sup>-4</sup> cm<sup>-2</sup>) [95], revealing a good crystalline quality. The authors assuming that the dislocation density could be reduced using their own wafer as substrates [94].
- (iii) Sumitomo electric also announced the fabrication of two inch GaN wafers with quite low (10<sup>4</sup>–10<sup>5</sup> cm<sup>-2</sup>) dislocation density areas about 500 μm in diameter. The free electron concentration was about 2 × 10<sup>18</sup> cm<sup>-3</sup> and the resistivity less than 2 × 10<sup>-2</sup> Ω cm. No detailed were however given about the fabrication process.

The development of GaN in both routes bulk growth and thin film epitaxial growth techniques film appear an important challenge involving different domains of applications, (electronics for high power, high temperature applications [96], optoelectronic devices [97], spintronic applications [98]). In addition during these last years a lot of research activity was trapped both by the preparation of GaN nanocrystallites, different applications requiring nano particles with a high crystalline quality and an appropriated shape (nano-wires (1D), nanoplatelets (2D), nanocube (3D) or the GaN deposition of thin films [99–112]).

Consequently GaN and the derived materials would be one of the key materials for developing new devices.

## References

- [1] J.Y. Duboz, GaN as Seen by the Industry, C.R.A.S., tl, serie IV, 2000. p. 71.
- [2] S. Nakamura, in: B. GIL (Ed.), III-V Nitride-Based Short-Wavelength LEDs et LDs Group III Nitride Semiconductor Compounds—Physics and Applications, Oxford Science Publication, 1998, p. 3916.
- [3] L. Liu, J.H. Edgar, Substrates for gallium nitride epitaxy, Mater. Sci. Eng. R 37 (3) (2002) 61.
- [4] P.R. Hageman, V. Kirilyuk, W.H.M. Corbeek, J.L. Weyher, B. Lucznik, M. Bockowski, S. Porowski, S. Muller, Bulk and homoepitaxial GaN-growth and characterizations, J. Cryst. Growth 255 (2003) 241.
- [5] S. Porowski, Thick GaN layers grown by hydride vapor-phase epitaxy: hetero- versus homo-epitaxy, J. Cryst. Growth 189/190 (1998) 153.
- [6] C. Krichner, V. Schwegler, F. Eberhard, M. Kamp, K.J. Ebeling, P. Pystawko, M. Leszczynski, I. Grzegory, S. Porowski, MOVPE homoepitaxy of high-quality GaN: crystal growth and devices, Prog. Cryst. Growth Charact. 41 (2000) 57.
- [7] N. Grandjean, J. Massies, I. Grzegory, S. Porowski, GaN/AlGaIn quantum well for UV emission: heteroepitaxy versus homoepitaxy, Semicond. Sci. Technol. 16 (2001) 358.
- [8] P. Pystawko, R. Czernecki, M. Leszczynski, P. Perlin, P. Wisniewski, L. Dmowski, H. Teisseyre, T. Suski, I. Grzegory, M. Bockowski, G. Nowak, S. Porowski, Blue-Laser structures grown on bulk GaN crystals, Phys. Stat. Sol. A 192 (2) (2002) 320.
- [9] J.A. Van Vechten, Quantum dielectric theory of electronegativity in covalent systems. III. Pressure–temperature phase diagrams, heats of mixing, and distribution coefficients, Phys. Rev. B 7 (4) (1973) 1479.
- [10] J. Karpinski, J. Jun, S. Porowski, Equilibrium pressure of N<sub>2</sub> over GaN and high pressure solution growth of GaN, J. Cryst. Growth 66 (1984) 1.

- [11] W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, O. Shimomura, Congruent melting of gallium nitride at 6 GPa and its application to single crystal growth, *Nat. Mater.* 2 (2003) 735.
- [12] S. Porowski, High pressure crystallization of III-V nitrides, *Acta Physica Polonica.* 87 (2) (1995) 295.
- [13] H. Yamane, M. Shimada, S.J. Clarke, F.J. Disalvo, Preparation of GaN single crystals using a Na flux, *Chem. Mater.* 9 (1997) 413.
- [14] J.W. Kolis, S. Wilcenski, R.A. Laudise, Material chemistry and bulk crystal growth of group III nitrides in supercritical ammonia, *Mater. Res. Soc. Symp. Proc.* 495 (1998) 367.
- [15] B. Raghthamachar, W.M. Vetter, M. Dudley, R. Dalmau, R. Schelesser, Z. Sitar, E. Michaels, J.W. Kolis, Synchrotron white beam topography characterization of physical vapor transport grown AlN and ammonothermal GaN, *J. Cryst. Growth* 246 (2002) 271.
- [16] J. Karpinski, S. Porowski, High pressure vapor growth of GaN, *J. Cryst. Growth* 56 (1982) 77.
- [17] J. Karpinski, J. Jun, S. Porowski, Equilibrium pressure of N<sub>2</sub> over GaN and high pressure solution growth of GaN, *J. Cryst. Growth* 66 (1984) 1.
- [18] R. Madar, G. Jacob, J. Hallais, R. Fruchart, High pressure solution growth of GaN, *J. Cryst. Growth* 31 (1975) 197.
- [19] I. Grzegory, M. Bockowski, J. Jun, P. Figurny, On the liquidus curve of GaN, *High Pressure Res.* 7/8 (1991) 284.
- [20] P. Perlin, I. Gorczyca, N.E. Christensen, I. Grzegory, H. Teisseyre, T. Suski, Pressure studies of gallium nitride: crystal growth and fundamental electronic properties, *Phys. Rev. B* 45 (23) (1992) 13307.
- [21] M. Leszczynski, I. Grzegory, M. Bockowski, X-ray examination of GaN single crystals grown at high hydrostatic pressure, *J. Cryst. Growth* 126 (1993) 601.
- [22] I. Grzegory, J. Jun, S. Krukowski, M. Bockowski, S. Porowski, Crystal growth of III-N compounds under high pressure of nitrogen, *Physica B.* 185 (1993) 99.
- [23] S. Porowski, Growth and properties of single crystalline GaN substrates and homoepitaxial layers, *Mater. Sci. Eng. B* 44 (1997) 407.
- [24] S. Porowski, M. Bockowski, B. Lucznik, M. Wroblewski, S. Krukowski, I. Grzegory, M. Leszczynski, G. Nowak, K. Pakula, J. Baranowski, GaN crystal growth in increased volume high pressure reactors, *Mater. Res. Symp. Proc.* 449 (1997) 35.
- [25] I. Grzegory, M. Bockowski, B. Lucznik, S. Krukowski, M. Wroblewski, S. Porowski, Recent results in the crystal growth of GaN at high pressure, *MRS Internet J. Nitride Semicond. Res.* 1 (1996), art 20.
- [26] I. Grzegory, High nitrogen pressure growth of GaN crystal and their applications for epitaxy of GaN-based structures, *Mater. Sci. Eng. B* 82 (2001) 30.
- [27] I. Grzegory, High pressure crystallization of GaN for electronic applications, *J. Phys. Condens. Matter.* 14 (2002) 11055.
- [28] I. Grzegory, M. Bockowski, B. Lucznik, S. Krukowski, Z. Romanowski, M. Wroblewski, S. Porowski, Mechanism of crystallization of bulk GaN from the solution under high N<sub>2</sub> pressure, *J. Cryst. Growth* 246 (2002) 177.
- [29] M. Leszczynski, I. Grzegory, H. Teisseyre, T. Suski, M. Bockowski, J. Jun, J.M. Baranowski, S. Porowski, J. Dodmagala, The microstructure of gallium nitride monocrystals grown at high pressure, *J. Cryst. Growth* 169 (1996) 235.
- [30] K. Saarinen, T. Laine, S. Kuisma, J. Nissilä, P. Hautajärvi, L. Dobrzynski, J.M. Baranowski, K. Pakula, R. Stepniowski, M. Wojdak, A. Wyszomolek, T. Suski, M. Leszczynski, I. Grzegory, S. Porowski, Observation of native Ga vacancies in GaN by positron annihilation, *Phys. Rev. Lett.* 79 (16) (1997) 3030.
- [31] M. Lefeld, I. Frymark, Extended defects in GaN single crystals, *J. Phys. D Appl. Phys.* 34 (2001) A148.
- [32] Z. Liliental-Weber, J. Jasinski, J. Washburn, Comparison between structural properties of bulk GaN grown in liquid Ga under N<sub>2</sub> pressure and GaN grown by other methods, *J. Cryst. Growth* 246 (2002) 259.
- [33] J.L. Weyher, I. Match, G. Kamler, J. Borysiuk, I. Grzegory, Characterization of GaN single crystals by defects-selective etching, *Phys. Stat. Sol. C* 3 (2003) 821.
- [34] E. Frassinetti, W. Knap, S. Krukowski, P. Perlin, P. Wisniewski, T. Suski, I. Grzegory, P. Porowski, Evidence of free carrier concentration along the c-axis for undoped GaN single crystals, *J. Cryst. Growth* 230 (2001) 442.
- [35] S. Krukowski, M. Bockowski, B. Lucznik, I. Grzegory, S. Porowski, T. Suski, M. Wroblewski, High nitrogen pressure growth of GaN single crystals: doping and physical properties, *J. Phys. Condens. Matter.* 13 (2001) 8881.
- [36] S. Porowski, Near defect free GaN substrates, *MRS Internet J. Nitride Semi-Cond. Res.* 4\$1 (1999), art 1.3.
- [37] S. Porowski, Bulk homoepitaxial GaN-growth characterization, *J. Cryst. Growth* 189/190 (1998) 153.
- [38] R. Piotrkowski, E. Litwin-Staszewska, T. Suski, I. Grzegory, Study of dopant activation in bulk GaN:Mg, *Physica B* 308–310 (2001) 47.
- [39] T. Suski, E. Litwin-Staszewska, P. Perlin, P. Wisniewski, H. Teisseyre, I. Grzegory, M. Bockowski, S. Porowski, K. Saarinen, J. Nissila, Optical and electrical properties of Be doped GaN bulk crystals, *J. Cryst. Growth* 230 (2001) 368.

- [40] M. Bockowski, Growth and doping of GaN and AlN single crystals under high pressure of nitrogen, *Cryst. Res. Technol.* 36 (8–10) (2001) 771.
- [41] I. Grzegory, M. Bockowski, B. Lucznik, M. Wroblewski, H. Teisseyre, J. Borysiuk, S. Porowski, Seeded growth of GaN at high N<sub>2</sub> pressure on (0001) polar surface of GaN single crystalline substrates, *Mater. Sci. Semi-Conduct. Process* 4 (2001) 525.
- [42] M. Bockowski, I. Grzegory, S. Krukowski, B. Lucznik, M. Wroblewski, G. Kamler, J. Borysiuk, P. Kwiatkowski, K. Jasik, S. Porowski, Gallium nitride growth on sapphire/GaN templates at high pressure and high temperatures, *J. Cryst. Growth* 274 (2005) 55.
- [43] M. Bockowski, I. Grzegory, J. Borysiuk, G. Kamler, B. Lucznik, M. Wroblewski, P. Kwiatkowski, K. Jasik, S. Krukowski, S. Porowski, Growth of GaN on patterned GaN/sapphire substrates by high pressure solution method, *J. Cryst. Growth* 281 (2005) 11.
- [44] J.L. Weyher, G. Kamler, G. Nowak, J. Borysiuk, B. Lucznik, M. Krysko, I. Grzegory, S. Porowski, Defects in GaN single crystals and homoepitaxial structures, *J. Cryst. Growth* 281 (2005) 135.
- [45] T. Inoue, Y. Seki, O. Oda, S. Kurai, Y. Yamada, T. Taguchi, Growth of bulk GaN single crystals by the pressure-controlled solution method, *Jpn. J. Appl. Phys. Part 1* 39 (4B) (2000) 2394.
- [46] T. Inoue, Y. Seki, O. Oda, S. Kurai, Y. Yamada, T. Taguchi, Growth of bulk GaN crystals by the pressure-controlled solution method, *J. Cryst. Growth* 229 (2001) 35.
- [47] T. Inoue, Y. Seki, O. Oda, S. Kurai, Y. Yamada, T. Taguchi, Pressure-controlled solution growth of bulk GaN crystals under high pressure, *Phys. Stat. Sol. B* 223 (15) (2001) 15.
- [48] H. Yamane, M. Shimada, T. Sekiguchi, F.J. Disalvo, Morphology and characterization of GaN single crystals grown in a Na flux, *J. Cryst. Growth* 186 (1998) 6.
- [49] H. Yamane, M. Shimada, T. Endo, F.J. Disalvo, Polarity of GaN single crystals prepared with a Na flux, *Jpn. J. Appl. Phys. Part 1* 37 (6) (1998) 3436.
- [50] H. Yamane, D. Kinno, M. Shimada, F.J. Disalvo, Crystal growth of GaN from Na–Ga melt in BN container, *J. Ceram. Soc. Jap.* 107 (10) (1999) 925.
- [51] H. Yamane, D. Kinno, M. Shimada, T. Sekiguchi, F.J. Disalvo, GaN single crystals from a Na–Ga melt, *J. Mater. Sci.* 35 (2000) 801.
- [52] M. Aoki, H. Yamane, M. Shimada, T. Sekiguchi, T. Hanada, T. Yao, S. Sarayama, F.J. Disalvo, Growth of GaN from a Na–Ga melt at 750 °C and 5 MPa of N<sub>2</sub>, *J. Cryst. Growth* 218 (2000) 7.
- [53] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, F.J. Disalvo, Growth of 5 mm GaN single crystals at 750 °C from a Na–Ga melt, *Cryst. Growth Design* 1 (2) (2001) 119.
- [54] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, F.J. Disalvo, GaN single crystals growth using high purity Na as a flux, *J. Cryst. Growth* 242 (2002) 70.
- [55] B.J. Shromme, K. Palle, C.D. Poweleit, H. Yamane, M. Aoki, F.J. Disalvo, Optical characterization of bulk GaN grown by the Na–Ga melt technique, *J. Cryst. Growth* 246 (2002) 299.
- [56] M. Aoki, H. Yamane, M. Shimada, T. Kajiwara, S. Sarayama, F.J. Disalvo, Morphology and polarity of GaN single crystals synthesized by the a Na flux method, *Cryst. Growth Design* 2 (1) (2002) 33.
- [57] M. Yano, M. Okamoto, Y. Khin, M. Yoshimura, Y. Mori, T. Sasaki, Control of nucleation site and growth orientation of bulk GaN crystals, *Jpn. J. Appl. Phys. Part 2* 38 (10A) (1999) L1121.
- [58] F. Kawamura, T. Iwahashi, K. Omae, M. Morishita, M. Yoshimura, Y. Mori, T. Sasaki, Growth of large GaN single crystals using the liquid phase epitaxy (LPE) technique, *Jpn. J. Appl. Phys. Part 2* 42 (1A/B) (2003) L4.
- [59] T. Iwahashi, F. Kawamura, M. Morishita, Y. Kai, M. Yoshimura, Y. Mori, T. Sasaki, Effect of ammonia threshold pressure and seed growth for bulk GaN single crystals by Na flux method, *J. Cryst. Growth* 237–239 (2002) 2112.
- [60] F. Kawamura, M. Morishita, K. Omae, M. Yoshimura, Y. Mori, T. Sasaki, Novel liquid phase epitaxy (LPE) growth method for growing large GaN single crystals: introduction of the flux film coated-liquid phase epitaxy (FFC-LPE) method, *Jpn. J. Appl. Phys. Part 2* 42 (8A) (2003) L879.
- [61] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, F.J. Disalvo, Condition for seeded growth of GaN crystals by the Na flux method, *Mater. Lett.* 56 (2002) 660.
- [62] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, H. Iwata, F.J. Disalvo, Dissolution and recrystallization of GaN in molten Na, *Jpn. J. Appl. Phys. Part 1* 42 (12) (2003) 7272.
- [63] H. Yamane, T. Kajiwara, T. Sekiguchi, M. Shimada, Zinc-blend-type cubic GaN single crystals prepared in a potassium flux, *Jpn. J. Appl. Phys. Part 2* 39 (2B) (2000) L146.
- [64] H. Yamane, M. Shimada, F.J. Disalvo, Growth of zinc-blend-type structure GaN from a Na–Ga melt, *Mater. Lett.* 42 (2000) 66.

- [65] Y. Song, W. Wang, W. Yuan, X. Wu, X.L. Chen, Bulk GaN single crystal: growth condition by flux method, *Mater. Res. Bull.* 35 (2000) 2325.
- [66] F. Kawamura, M. Morishita, T. Iwahashi, M. Yoshimura, Y. Mori, T. Sasaki, Synthesis of bulk GaN single crystals using Na-Ca flux, *Jpn. J. Appl. Phys. Part 2* 41 (12B) (2002) L1440.
- [67] F. Kawamura, T. Iwahashi, M. Morishita, K. Omae, M. Yoshimura, Y. Mori, T. Sasaki, Growth of transparent, large size GaN single crystals with low dislocations using Na-Ca flux system, *Jpn. J. Appl. Phys. Part 2* 42 (7A) (2003) L729.
- [68] M. Morishita, F. Kawamura, T. Iwahashi, M. Yoshimura, Y. Mori, T. Sasaki, Growth of bulk GaN single crystals Li-Na mixed flux system, *Jpn. J. Appl. Phys. Part 2* 42 (6A) (2003) L565.
- [69] B.N. Feigelson, R.L. Henry, Growth of GaN crystals from molten solution with Ga free solvent using a temperature gradient, *J. Cryst. Growth* 281 (2005) 5.
- [70] R. Dwilinski, A. Wyszomolek, J. Baranowski, M. Kaminska, R. Doradzinski, J. Garczynski, L. Sierzputowski, GaN synthesis by ammonothermal method, *Acta Physica Polonica.* 88 (5) (1995) 833.
- [71] R. Dwilinski, J. Baranowski, M. Kaminska, R. Doradzinski, J. Garczynski, L. Sierzputowski, On GaN crystallization by ammonothermal method, *Acta Physica Polonica.* 90 (4) (1996) 763.
- [72] R. Dwilinski, R. Doradzinski, J. Garczynski, L. Sierzputowski, J. Baranowski, M. Kaminska, Exciton photoluminescence of GaN bulk crystals grown by the AMMONO method, *Mater. Sci. Eng. B* 50 (1997) 46.
- [73] M. Placzewska, B. Suchanek, R. Dwilinski, K. Pakua, A. Wagner, M. Kaminska, Paramagnetic defects in GaN, *MRS Internet J. Nitride Semicond. Res.* 3 (1998), article 45.
- [74] C. Collado, G. Demazeau, B. Berdeu, A. Largeau, W. Lai-Tiong, A new route for the synthesis of nitrides: the solvothermal preparation of GaN, *High Pressure Res.* 18 (2000) 221.
- [75] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, H. Iwata, F. DiSalvo, Single crystal growth of GaN by the temperature gradient Na flux-method, *J. Cryst. Growth* 266 (2004) 461.
- [76] Q.S. Chen, V. Prasad, W.R. Hu, Modeling of ammonothermal growth of nitrides, *J. Cryst. Growth* 258 (2003) 181.
- [77] A. Denis, C. Labrugère, E. Gaudin, M. Lahaye, F. Dartigues, A. Largeau, G. Goglio, G. Demazeau, Evaluation of the solvothermal crystal growth of GaN using  $\text{Li}_3\text{GaN}_2$  as a nutrient and ammonia as a solvent, submitted for publication.
- [78] W.J. Wang, X.L. Chen, Y.T. Song, W.X. Yuan, Y.G. Cao, X. Wu, Assessment of Li-Ga-N ternary system and GaN single crystal growth, *J. Cryst. Growth* 264 (2004) 13.
- [79] T. Hashimoto, K. Fujito, B.A. Haskell, P.T. Fini, J.S. Speck, S. Nakamura, Growth of gallium nitride via fluid transport in supercritical ammonia, *J. Cryst. Growth* 275 (2005) e525.
- [80] D.R. Ketchum, J.W. Kolis, Crystal growth of gallium nitride in supercritical ammonia, *J. Cryst. Growth* 222 (2001) 431.
- [81] A.P. Purdy, Ammonothermal synthesis of cubic gallium nitride, *Chem. Mater.* 11 (1999) 1648.
- [82] A.P. Purdy, Ammonothermal recrystallization of gallium nitride with acidic mineralizer, *Cryst. Growth Design* 2 (2) (2002) 141.
- [83] A.P. Purdy, A.C. Cas, N. Muratore, Synthesis of GaN by high pressure ammonolysis of gallium triiodide, *J. Cryst. Growth* 252 (2003) 136.
- [84] M.J. Callahan, B. Wang, L.O. Bouthillette, S.Q. Wang, J.W. Kolis, D.F. Bliss, Growth of GaN crystals under ammonothermal conditions, *Mater. Res. Soc. Symp. Proc.* 798 (2004), y2. 10.1.
- [85] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Zener model description of ferromagnetism in zinc-blende magnetic semiconductors, *Science* (2000) 287.
- [86] T. Szyszko, G. Kamler, B. Strojek, G. Weisbrod, S. Podsiadlo, L. Adamowicz, W. Gebicki, J. Szczytko, A. Twardowski, K. Sikorski, Growth of bulk  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  single crystals, *Crystal Growth* 233 (2001) 631.
- [87] P. Geiser, J. Jun, S.M. Kazakov, P. Wägli, J. Karpinski, B. Batlogg, L. Klemm,  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  bulk single crystals, *Appl. Phys. Lett.* 86 (2005) 081908.
- [88] F. Iwasaki, H. Iwasaki, Historical review of quartz crystal growth, *J. Cryst. Growth* 237–339 (2002) 820.
- [89] V. Sukhovev, V. Ivantsov, Y.U. Melnik, A. Davydov, D. Tsvetkov, K. Tsvetkova, I. Nikitina, A. Zubrilov, A. Lavrentiev, V. Dimitriev, Characterization of 2.5-Inch diameter bulk GaN grown from the melt-solution, *Phys. Stat. Sol. A* 188 (1) (2001) 411.
- [90] V.A. Ivantsov, V.A. Sukhovev, V.A. Dimitriev, GaN crystals grown from a liquid phase at reduced pressure, *Mater. Res. Soc. Proc.* 468 (1997) 143.
- [91] M. Albrecht, M. Nerding, H.P. Strunk, V.A. Ivantsov, V. Sukhoveev, V.A. Dimitriev, Structure and optical properties of GaN crystals grown from the liquid phase, *MRS 2000. Fall Meeting Boston.*

- [92] R.P. Vaudo, G.R. Brandes, J.S. Flynn, X. Xu, M.F. Chriss, C.C. Christos, D.M. Keogh, F.D. Tamweber, Synthesis and properties of HVPE nitride substrates, in: Proc. Int. Workshop on Nitride Semiconductors, IPAP Conference Series, vol. 18, Japan, (2000), p. 15.
- [93] X. Xu, R.P. Vaudo, C. Loria, A. Salant, G.R. Brandes, J. Chaudhuri, Growth and characterization of low defect GaN by hybride vapor phase epitaxy, *J. Cryst. Growth* 246 (2002) 223.
- [94] X. Xu, R.P. Vaudo, G.R. Brandes, Fabrication of GaN wafer for electronic and optoelectronic devices, *Opt. Mater.* 23 (2003) 1.
- [95] R.P. Vaudo, X. Xu, C. Loria, A.D. Salant, J.S. Flynn, G.R. Brandes, GaN boule Growth, a pathway to GaN wafer with improved material quality, *Phys. Stat. Sol. A* 194 (2002) 494.
- [96] S.J. Pearton, F. Ren, A.P. Zhang, G. Dang, X.A. Cao, K.P. Lee, H. Cho, B.P. Gila, J.W. Johnson, C. Monier, C.R. Abernathy, J. Han, A.G. Baca, J.I. Chyi, C.M. Lee, T.E. Nee, C.C. Chuo, S.N.G. Chu, GaN electronics for high power, high temperature applications, *Mater. Sci. Eng. B* 82 (2001) 227.
- [97] R. Triboulet, A. Rogalski, Materials science and applications of solid crystals III-V Review, *Adv. Semiconductor Mag.* 14 (2) (2001) 46.
- [98] S.J. Pearson, C.R. Abernathy, M.E. Overberg, G.T. Thaler, A.H. Onstine, B.P. Gila, F. Ren, B. Lou, J. Kim, New applications for gallium nitride, *Mater. Today* (June, 2002) 24.
- [99] J.F. Janik, R.L. Wells, Gallium imide ( $(\text{Ga}/\text{NH}_3)_{3/2}$ )m a New Polymeric Precursor for gallium nitride powders, *Chem. Mater.* 8 (1996) 2708.
- [100] Y. Xie, Y. Qian, W. Wang, S. Zhang, Y. Zhang, A benzene-thermal synthetic route to nanocrystalline GaN, *Science* 272 (1996) 1926.
- [101] K.E. Gonsalves, S.P. Rangarajan, G. Carlson, Optical and microstructural characterization of chemically synthesized gallium nitride powders, *Appl. Phys. Lett.* 71 (1997) 2175.
- [102] D.I. Micic, S.P. Ahrenkiel, D. Bertram, A.J. Nozik, Synthesis structure and optical properties of colloidal GaN quantum dots, *Appl. Phys. Lett.* 75 (1999) 478.
- [103] A. Manz, A. Birkner, M. Kolbe, R.A. Fisher, Solution synthesis of colloidal gallium nitride at unprecedented low temperature, *Adv. Mater.* 12 (2000) 569.
- [104] L. Grocholl, J. Wang, E.G. Gillan, Solvothermal azide decomposition route to GaN nanoparticles, nanorods, and faceted crystallites, *Chem. Mater.* 13 (2001) 4290.
- [105] M. He, et al., Growth of GaN nanowires by direct reaction of Ga with  $\text{NH}_3$ , *J. Cryst. Growth* 231 (2001) 357.
- [106] J.Q. Hu, B. Deng, W.X. Zhang, K.B. Tang, Y.T. Qian, Gallium nitride synthesis from sodium azide using iodine as a heat sink and diluent, *Chem. Phys. Lett.* 351 (2002) 229.
- [107] K. Sardar, C.N.R. Rao, New Solvothermal routes for GaN nanocrystals, *Adv. Mater.* 16 (2004) 425.
- [108] V. Srivastava, V. Sureshlumar, P. Puviasaru, K. Thangaraju, R. Thangavel, J. Kumar, Growth and characterization of gallium nitride nanowire, *J. Cryst. Growth* 275 (1–2) (2005) e2367.
- [109] D.M. Hoffman, Chemical vapour deposition of nitride thin films, *Polyhedron* 13 (1994) 1169.
- [110] M. Bockowski, I. Grzegory, S. Krukowski, B. Lucznik, M. Wroblewski, G. Kamler, J. Borysiuk, P. Kwiatkowski, K. Jasik, S. Porowski, Deposition of bulk GaN from solution in gallium under high  $\text{N}_2$  pressure on silicon carbide and sapphire substrates, *J. Cryst. Growth* 270 (2004) 409.
- [111] E.H. Park, J.S. Park, T.K. Yoo, As grown p-type GaN growth by dimethylhydrazine nitrogen precursor, *J. Cryst. Growth* 272 (2004) 426.
- [112] H. Nagayoshi, S. Nishimura, T. Takeuchi, M. Hirai, K. Terashima, GaN growth using gallium hydride generated by hydrogenation of liquid gallium, *J. Cryst. Growth* 275 (2005) e1007.