

Pressure grown GaN-crystal growth and applications

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The current status of bulk pressure grown GaN substrates and the lasers on them is summarized. Gallium nitride crystals grown from high temperature (~1500 °C) solutions in gallium at high pressure (~10-15 kbar) of N₂ gas are usually almost free of dislocations (10-100 dislocations per cm²). Therefore, the construction of blue-violet lasers based on the epitaxial structures grown by both MOCVD and MBE methods on the pressure-grown substrates is possible. The crystals grown routinely by this method are limited in both their lateral size (up to about 10 mm) and their thickness (about 100 μm). Relatively large (exceeding 1 cm) GaN single crystalline platelets can be grown on free gallium surfaces which are in contact with N₂ gas. It is shown that for solution growth of GaN on GaN substrates, macroscopically flat and uniform crystallization fronts can be obtained, even for very long processes, by the creation of a convection free zone at the growing surface. Due to a very uniform crystallization front achieved in the high pressure solution growth of GaN on GaN/sapphire substrates, the epitaxial lateral overgrowth (ELOG) became possible. The dislocation densities in the material resulting from lateral growth were in the range of 10⁵-10⁶ cm⁻², that is 2 to 3 orders of magnitude lower than in the initial GaN. The GaN platelets grown under pressure were used as substrates for hydride vapor phase epitaxy (HVPE) which allows very fast growth of GaN in the c-direction. In this way single crystals of GaN with a thickness of about 2 mm were grown. These crystals were sliced along non-polar crystallographic planes. Then both {1 1 2 0} (non-polar) and {0 0 0 1} (polar) oriented platelets have been used for the epitaxial growth of GaN/AlGaIn multi quantum wells by molecular beam epitaxy (MBE). According to the expectations, much stronger UV emission was obtained from the "non-polar" multi quantum wells at room temperature. The character of the low temperature photoluminescence spectra confirmed high structural quality of these samples.

Key words: GaN single crystals, high pressure solution growth, HVPE of GaN, GaN based lasers by MOCVD, GaN based lasers by MBE.

Introduction

The melting temperatures and pressures of most typical semiconductor materials are compared in Table 1. The melting temperature of GaN has been calculated in 1973 by the use of Van Vechten's Quantum Dielectric Theory of Chemical Bonding [1]. The corresponding pressure followed from the extrapolation of the experimental equilibrium data [2, 3]. Only recently, the melting conditions for GaN have been determined experimentally by the *in situ* X-ray - high pressure - high temperature measurements performed at the Synchrotron Radiation Research Center of Japan Atomic Energy Research Institute by Utsumi *et al.* [4]. The Table shows that both temperature and pressure at melting of GaN are much higher than for typical semiconductors.

Due to these extreme melting conditions, GaN (like AlN and InN) cannot be grown from its stoichiometric melt by methods commonly used for typical semiconductors. This was the main reason for the relatively late development of GaN-based optoelectronic and electronic

devices, despite the outstanding physical properties of this material. Due to elaboration of the two-step Metal Organic Chemical Vapor Deposition (MOCVD) processes for the growth of both n- and p-type (GaAlIn)N epitaxial structures on highly mismatched sapphire substrates [i.e. 5, 6] GaN became the basic material for short wavelength optoelectronics and for the high power high temperature electronic devices. At present, high brightness blue and green light emitting diodes (LEDs) and low power blue laser diodes (LDs) are commercially available [5]. Nevertheless the lack of defect free, lattice matched and available substrates for GaN-based epitaxial structures is still a serious obstacle

Table 1. Melting conditions of semiconductors

crystal	T ^M , °C	p ^M , atm.
Si	1400	< 1
GaAs	1250	15
GaP	1465	30
GaN	2520 2220	45000* 60000**
diamond (synthesis)	1600	60000

*theoretical estimation by Van Vechten [1], pressure extrapolated from the experimental equilibrium data of [2, 3]

**experiment reported in [4]

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in the further development of some important optoelectronic and electronic devices. For instance, the presence of structural defects in structures deposited on foreign substrates impedes extension of the power and the lifetime of the blue-violet InGaN based lasers. Recently, considerable effort has been devoted to solving the problem of the substrate for III-V nitrides.

At present, the most important approach to obtain relatively low defect density quasi-bulk GaN substrates is the use of Hydride Vapor Phase Deposition (HVPE) to grow thick (few hundreds of μm) GaN layers on foreign substrates [7-10]. Then the substrates can be removed [11-13] and large diameter free-standing GaN wafers can be obtained. Due to interactions between dislocations during the growth of the thick GaN layer, their density drops to values as low as 10^6 cm^{-2} [14]. Among these free-standing quasi-bulk GaN substrates the ones developed by Sumitomo Electric [15] enabled the first demonstration [16] of high power laser diodes and diode arrays. The method of the fabrication of the substrates is a multi-step deposition of GaN on GaAs wafers [17] including defect-selective etching of the nitride and subsequent re-growth on the surface containing the large pits being the result of the etching.

Several groups are working toward obtaining a large low defect density bulk GaN crystal. The method requiring temperatures and pressures much less extreme than are necessary for melting, is growth from solutions. At present, there are two basic approaches to the solution growth of GaN: crystallization from solutions in supercritical NH_3 [18, 19, 21] (the so called ammonothermal method) and crystallization from solutions in liquid gallium. Both methods require the use of high pressure. The typical pressure and temperature ranges for the ammonothermal method are 1-3 kbar and 400-600 °C respectively. Both the spontaneous growth resulting in a few mm size crystals and the

growth seeded with the free standing HVPE-GaN wafers have been studied. The main problems encountered in this approach is the low growth rates of the order of 0.1 mm per day. The acceleration of the growth has been reported [18] for the ammonothermal processes performed at pressures as high as 20 kbar.

The best structural quality GaN crystals are grown from solutions of atomic nitrogen in liquid gallium under high N_2 pressure. This technique has been extensively developed in the Institute of High Pressure Physics Polish Academy of Sciences (former High Pressure Research Center PAS), Warsaw, Poland [21, 22] and also, in the Japan Energy Corporation and Yamaguchi University [23].

In the following, the process of GaN crystallization from solutions of atomic nitrogen in liquid gallium under high N_2 pressure will be described on the basis of the results obtained in Warsaw. The most important problems encountered in this technique are strong anisotropy of the growth at the conditions allowing stable crystallization, difficult control of the nucleation rates on the polar $\{0001\}$ surfaces and difficult control of the mass transport mechanisms in the growth solution. The method is developed by directional crystallization from solution on seeds and by HVPE.

High pressure solution growth of GaN-basic method

The simplest way to crystallize GaN from solution in liquid Ga metal is the growth in a temperature gradient without an intentional seeding [i.e. 21]. At the p-T conditions corresponding to the GaN stability range [2, 3], the solubility of nitrogen in gallium is an increasing function of temperature (Fig. 1a). So, if a temperature gradient is maintained in the system, crystal growth is observed in the cooler part of the solution, which is

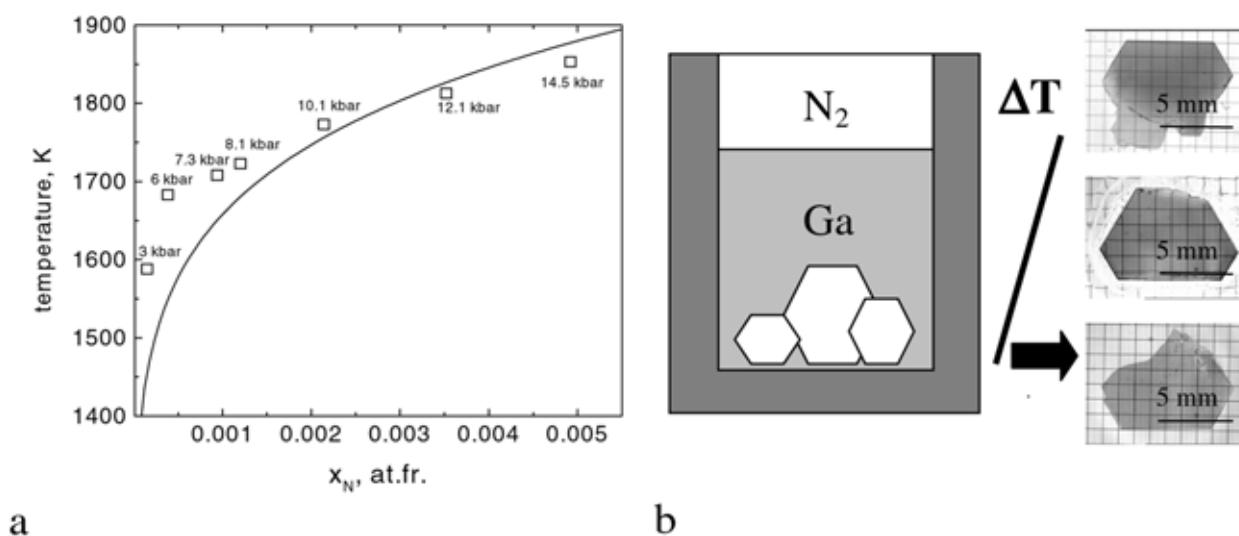


Fig. 1. Crystallization of GaN from solution in Ga: a-liquidus line for Ga-GaN system: the solid line was calculated with the ideal solution approximation, b-schematic illustration of the experimental arrangement. Typical GaN crystals are also shown.

schematically shown in Fig. 1b. The crystals are usually grown from the solutions in pure liquid gallium or in Ga alloyed with 0.2-0.5 at.% of Mg or Be at pressures in the range of 8-14 kbar and temperatures of 1400-1600°C, in 80-150 hours processes. Mg and Be as the most efficient acceptors in GaN are added to the growth solutions in order to reduce the concentration of free electrons in the crystals by compensation of residual donors. Thus the crystals can be highly conductive ($n > 10^{19} \text{ cm}^{-3}$) or highly resistive. As shown in Fig. 1b, the dominating shape of the crystals is hexagonal platelets. The lateral size of the routinely grown platelets is up to 10 mm whereas their thickness is 80-120 μm . This indicates a strong growth anisotropy in the conditions applied.

The significant increase of ΔT (i.e. up to 100 K) does not lead to a spectacular increase of the growth rates but rather to growth instabilities on the $\{0001\}$ polar surfaces of the crystals. The tendency for the unstable growth is stronger for one of the polar $\{0001\}$ faces of the platelets. On this side morphological features like macrosteps, periodic inclusions of solvent or cellular growth structures are observed. The opposite surface is mirror like and often atomically flat. For crystals grown without an intentional doping (strongly n-type) the unstable surface always corresponds to the Ga-polar (0001) face of GaN, whereas for crystals doped with Mg (semi-insulating-see next Section) it is always the opposite N-polar $[000\bar{1}]$ face. Therefore doping with Mg (if sufficient to compensate free electrons) changes microscopic growth mechanisms on the $\{0001\}$ polar surfaces of GaN.

The structure of the pressure grown crystals has been studied by the X-ray diffraction (XRD) [24], transmission electron microscopy (TEM) [25, 26] and defect selective etching (DSE) [27, 28]. The crystals can contain dislocations, micro-defects (arranged in narrow stripes in c-plane), inversion domains (occasionally), and impurity-related growth striations. The density of

dislocations as determined by DSE in molten KOH-NaOH, is usually very low and does not exceed 100 cm^{-2} . The result of DSE of a GaN/sapphire heteroepitaxial layer and a GaN pressure grown crystal is shown in Fig. 2a and 2b respectively. Due to the high structural perfection the crystals can be easily cleaved along $\langle 10\bar{1}0 \rangle$ directions (Fig. 1c) which is very useful for making mirrors for lasers.

Applications of the high pressure grown crystals

Despite their relatively small size, the GaN crystals grown in the temperature gradient without an intentional seeding are used as substrates for epitaxy and processed for making devices. The extremely low dislocation densities, easy cleaving and high electric conductivity are the main advantages compensating in some extent, the limited size of the crystals and making them suitable substrates for fabrication of blue-violet InGaN multi quantum wells-based laser diodes. The epitaxial structures of the separate confinement heterostructure lasers with AlGaIn cladding layers and Mg and Si doped GaN waveguides were grown by MOCVD [29]. Even for the growth without any special steps to match AlGaIn to the substrate, the final structures contained a very low number of dislocations (of about 10^5 cm^{-2}). It allowed one to fabricate pulsed current operated laser diodes of a high power output approaching 4 W in 50 ns pulse. Recently, the continuous wave operation has been achieved [30] due to the improved mounting providing better heat dissipation from the lasing structures. Figure 3a shows one of the GaN crystals with several laser diode chips (before separation). A set of the laser diodes separated from the crystal by cleaving is shown in Fig. 3b.

The use of the pressure-grown substrates allowed the first demonstration of the blue-violet laser diode grown by Plasma Assisted MBE [31]. Contrary to the common

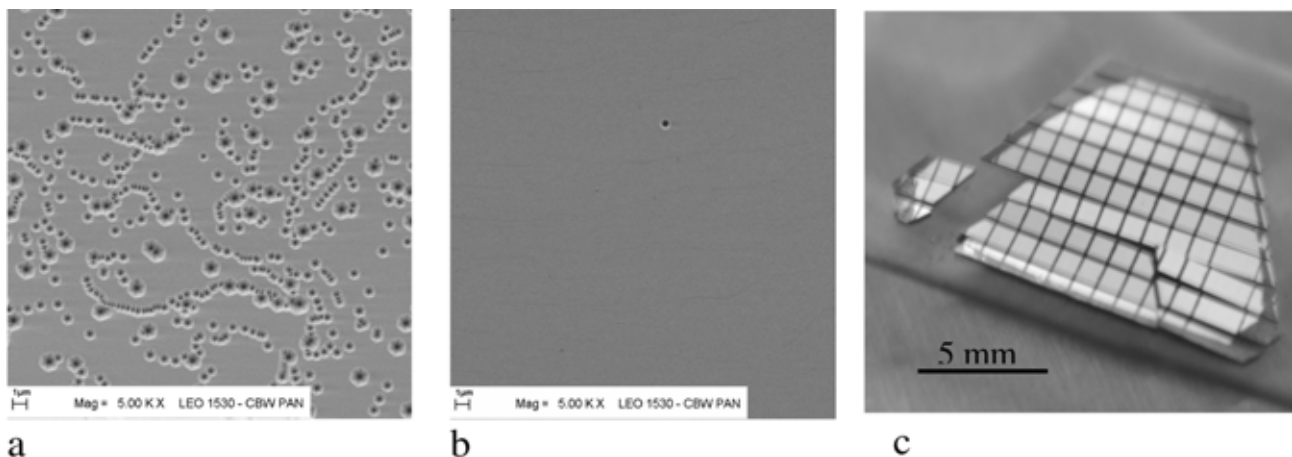


Fig. 2. Defect selective etching and cleaving of GaN: a-GaN/sapphire heteroepitaxial layer after DSE, b-GaN pressure grown crystal after DSE (Ga-polar surface), c-GaN crystal cleaved along $\langle 10\bar{1}0 \rangle$ directions.

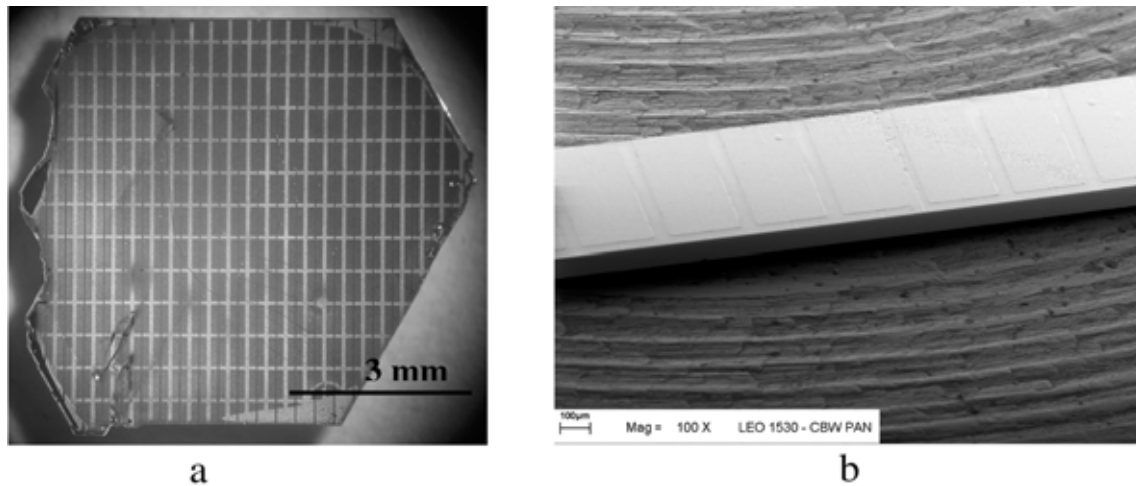


Fig. 3. Processing of the laser diodes grown on pressure grown GaN substrate: a-laser diode chips on the pressure grown substrate, b-set of laser diodes cleaved from the crystal.

belief, it was shown that a high quality full InGaN MQW based laser structure can be grown at a temperature as low as 710 °C. The laser operation at 408 nm was then demonstrated at room temperature with 50 ns pulses. The threshold current density and voltage were 9 kA/cm² and 8.2 V respectively. A high output power of 1.1 W per pulse has been achieved. This is a crucial result confirming that single crystalline lattice matched low dislocation density GaN substrates would open new possibilities in GaN-based optoelectronics.

The semi-insulating GaN:Mg substrates have been used to grow GaN/AlGaIn heterostructures with two dimensional electron gas (2DEG) by both plasma assisted and reactive (with ammonia) MBE [32, 33]. Very high mobilities of the 2D electron gas have been achieved by both methods. A Hall mobility for 2DEG

as high as 109 000 cm²/Vs at 1.5 K and over 2500 cm²/Vs at room temperature (the highest values reported for GaN/AlGaIn heterostructure) have been measured for samples grown by plasma assisted MBE.

Crystallization of GaN on the free Ga surface

Up to now, the “high pressure” crystals of the biggest lateral size have been grown on free gallium surfaces. In the case of the growth in a temperature gradient without an intentional seeding in the volume of the solution, the uniformity of the growth conditions is perturbed by several factors like: the temperature gradient maintained, convectional flows in the solution or the neighboring crystals. This can be avoided to some extent, with a free gallium surface in direct

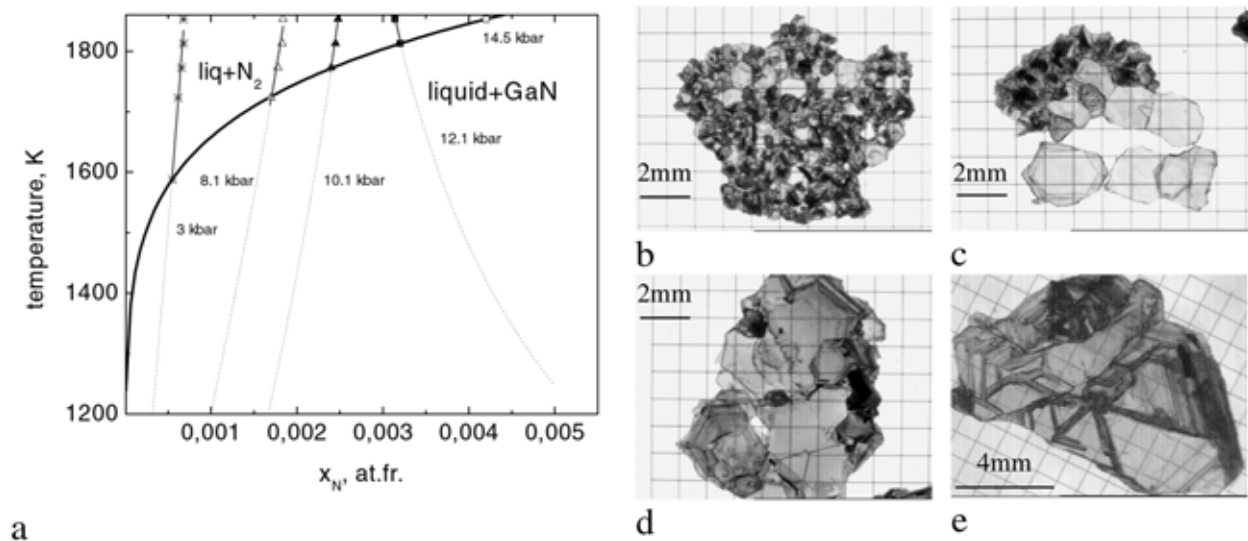


Fig. 4. Crystallization of GaN on free gallium surfaces: a-solubility of nitrogen in liquid gallium. Ga-N₂ isobars calculated, GaN-Ga solid curve calculated with the ideal solution approximation, b, c, d, e-GaN crust crystallized at 6 kbar ($T_{eq} = 1400^\circ\text{C}$), at supercoolings of 70°C, 40°C, 15°C and 10°C respectively.

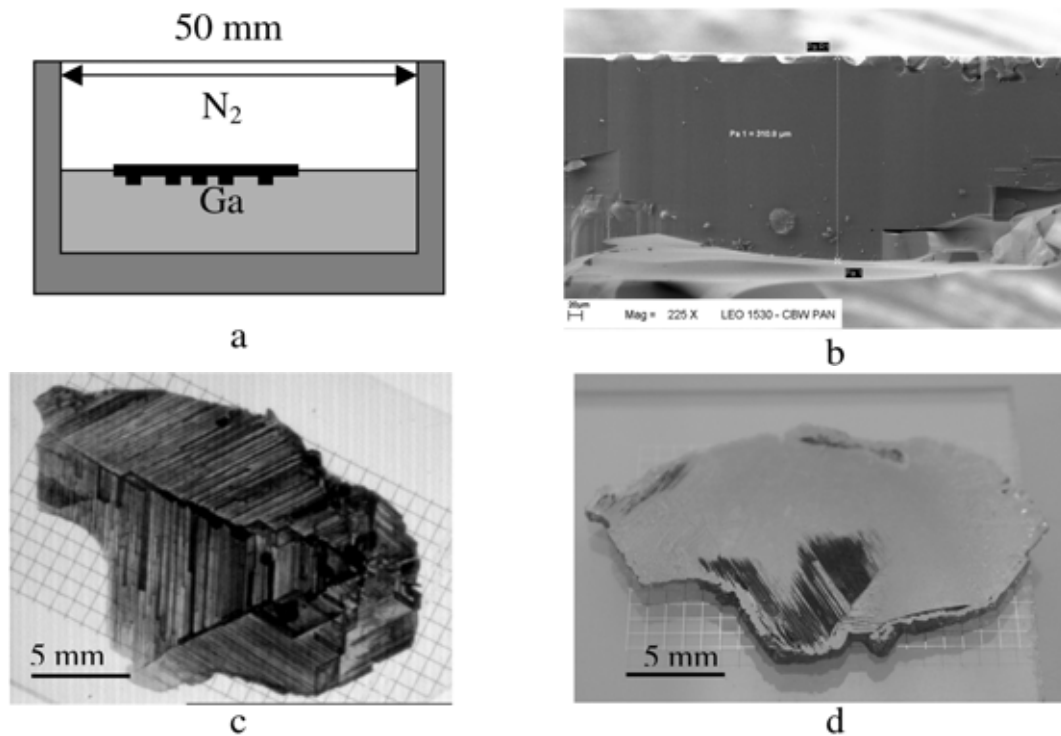


Fig. 5. Crystal growth of GaN on free Ga surfaces: a-schematic illustration of the process: the GaN crystal floating on the Ga surface with N-polar surface (upper) flat and Ga-polar surface destabilized, b-cross section of the GaN crystal used as substrate for solution growth on the N-polar (lower) surface at 1400°C: the opposite (upper), Ga-polar surface is decomposed being in contact with the N_2 gas at 2 kbar overpressure during 50 h., c-GaN crystal grown on the free Ga surface with unstable Ga-polar face, d-the same crystal after deposition of thick GaN layer on the N-polar surface (HVPE) and polishing of the Ga-polar one.

contact with compressed nitrogen, at quasi isothermal conditions. Until the metal surface is not covered with GaN, the solubility of N follows Ga- N_2 isobars [34] shown in Fig. 4a. If the N_2 pressure becomes higher (or the temperature lower than required for three phase equilibrium), the solution at the surface can be uniformly supersaturated. Then, nucleation and growth can be expected on the gallium surface. The final conditions for such a process starting from the conditions corresponding to Ga+ N_2 area of the phase diagram, can be created by lowering the temperature or increasing the pressure in the system. If the supersaturation is created by cooling, the surface crystallization should depend on the cooling rate, final supercooling, geometry and non-intentional temperature gradients in the system. We have shown that the result of the surface crystallization depends mainly on the final supercooling whereas the cooling rate in the range of 0.5-20 °C, is not crucial for this process. Typically, a GaN crystalline crust consisting of grains of different size was obtained in 50-100 h. processes. Examples of surface crystals grown at different supercooling, at 6 kbar are shown in Fig. 4bcde. At a small supercooling, single crystalline GaN with lateral size reaching 1-2 cm was quite often observed.

The “surface crystals” similar to the one shown in Fig. 4e are also hexagonal platelets. Usually, the N-polar surface is flat and directed towards the gas phase.

The Ga-polar surface directed to the liquid is morphologically unstable. Figure 5a shows this situation schematically. Such an arrangement of the crystal on the surface can be explained by a higher stability of the N-polar face of GaN against N_2 gas. For this face, the nitrogen atoms are bonded to the crystal by three bonds. For the Ga-polar face the N-atoms are bonded by single bonds thus the face becomes unstable at small N_2 overpressures. Figure 5b shows a GaN crystal used as a substrate for solution growth on a N-polar surface at a small N_2 overpressure. During the 50 h process the opposite, Ga surface being in direct contact with N_2 gas, decomposed developing new faces of inversed (stable) polarity.

The “surface crystals” are very thin and thus very difficult to further treatment. Since the N-polar face is flat, the thickness of the crystals can be increased by HVPE and then polished. Figure 5c shows a “surface crystal” as grown with the Ga-polar surface strongly unstable, whereas Fig. 5d shows the same crystal with a Ga-polar surface mechanically polished.

Solution growth of GaN on GaN/sapphire and GaN substrates

Since the high pressure crystallization from solution gives crystals with very small dislocation densities it is worth working on increasing their size using a modi-

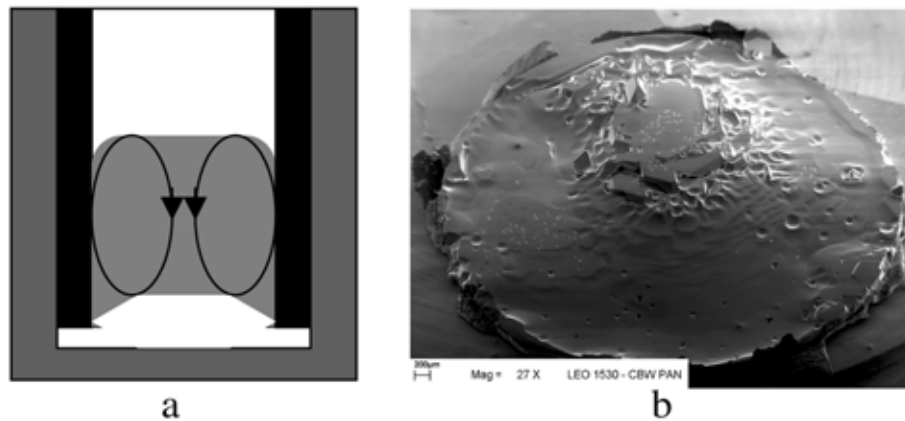


Fig. 6. Directional crystallization of GaN on GaN substrate in a temperature gradient in the simplest configuration: a-crucible with substrate and a new grown GaN with a non flat surface, b-GaN crystal with new grown GaN ($T_G = 1400^\circ\text{C}$, $\Delta T = 50^\circ\text{C}$, $t = 95\text{h}$), the crystallization front has a form of a single growth hillock.

fication of the same method. To increase the thickness of the pressure - grown GaN platelets the configuration shown schematically in Fig. 6a where the GaN platelet is used as substrate for the growth in the (0001) direction in a temperature gradient was applied. From our earlier studies [35] of this problem, it is known that such a directional crystallization is possible resulting again in high quality material regarding the presence of dislocations. On the other hand, the shape of the growing surfaces destabilized with time: the flatness and even the continuity of the new grown material was broken after a few tens of hours of growth. An example is shown in Fig. 6b. It was assumed that the main reason for the observed instability of the crystallization front was the non uniform distribution of nitrogen on the growth surface due to convection in the liquid.

Recently, experiments of this kind were re-started with a goal to stabilize the shape of the crystallization front in long duration processes. For these studies, GaN/sapphire substrates have been used in most experiments. The growth on the GaN/sapphire substrates in the simplest configuration of Fig. 6a also

resulted in unstable growth. Therefore, the configuration was modified by introducing a thin baffle plate close to the substrate (Fig. 7) to suppress convection in the crystallization zone. The shape of the growing surface improved immediately becoming flat for both natural (substrate on the bottom of the crucible-Fig. 7a) and reversed (substrate at the top of the crucible-Fig. 7b) temperature gradients. Layers up to $250\ \mu\text{m}$ thick have been grown on the substrates with diameters of 10 and 20 mm without deterioration of the crystallization front-Fig. 7c.

These layers were free of cracks and contained about 10^7 dislocations per cm^{-2} i.e. 1-2 orders of magnitude less than the initial substrate material.

The kinetics of the crystallization processes considered is studied (for details see [36]) for the configuration shown in Fig. 7b. The current results are collected in Fig. 8 where the dependencies of the average growth rate on time for 100°C supercooling (defined here as the temperature difference between hot and cold ends of the solution), with a maximum temperature in the system of 1450°C and supercooling for 100 h processes

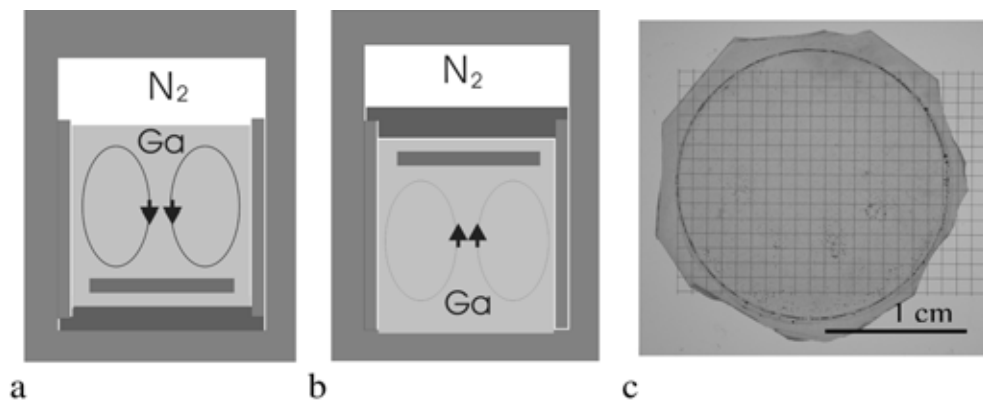


Fig. 7. Crystallization of GaN with a convection free zone: a- configuration with “natural” temperature gradient (substrate on the bottom), b-configuration with “reversed” temperature gradient (substrate at the top of the crucible, c-50 μm GaN layer grown on GaN/sapphire substrate in natural temperature gradient ($1350\text{-}1450^\circ\text{C}$) at 10 kbar N_2 pressure during 50 h.

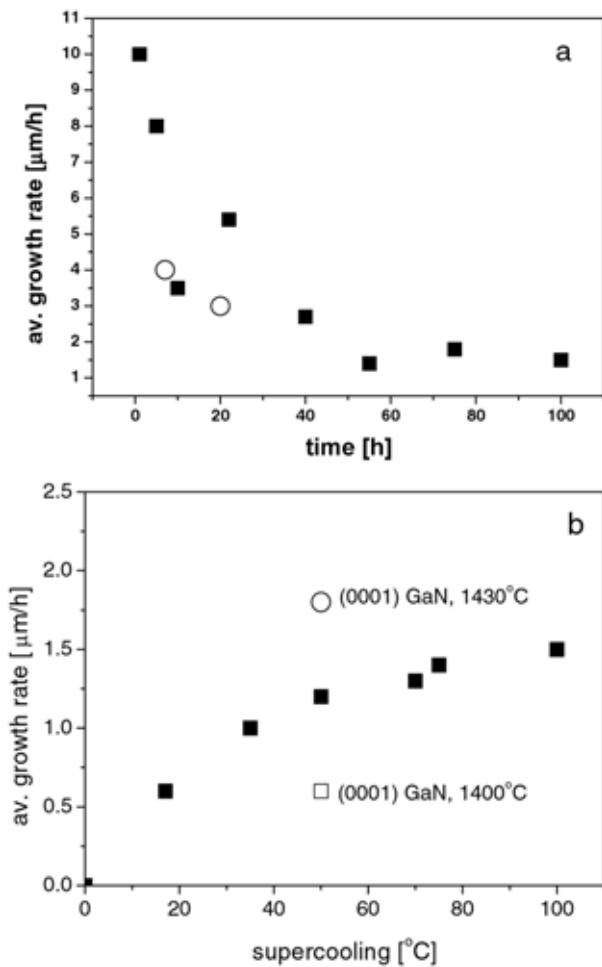


Fig. 8. Kinetics of the growth of GaN on GaN/sapphire substrates for a temperature of the hot end of the crucible of 1450 $^{\circ}\text{C}$: a-average growth rate vs. time at 100 $^{\circ}\text{C}$ supercooling, open circles for a GaN feed as source of nitrogen, otherwise N_2 dissolved directly, b-average growth rate vs. supercooling for 100 h. processes, open square: growth on GaN substrate at 1400-1450 $^{\circ}\text{C}$ temperature range, open circle: growth on GaN substrate at 1430-1480 $^{\circ}\text{C}$ temperature range.

are shown. The first diagram indicates that at the beginning of the growth, the growth rate is about 10 $\mu\text{m/h}$, then it decreases in time and saturates after about 50 h. of growth, at a constant level of about 1.5 $\mu\text{m/h}$. The most possible reason for this behavior is the gradual changes in the growth surface morphology. The supporting observations are that the growth on a GaN single crystal substrate with otherwise identical conditions was slower than on GaN/sapphire substrate (of high dislocation density) (shown in Fig. 8b) and that the addition of a small amount of indium to the growth solution increased the growth rate almost twice.

The diagram in Fig. 8b indicates that the growth rate increases with the supercooling with a tendency to saturate at higher supercooling levels. This tendency however is most probably, due to decreasing the temperature of crystallization since in this series of experiments the temperature of the hot end of the

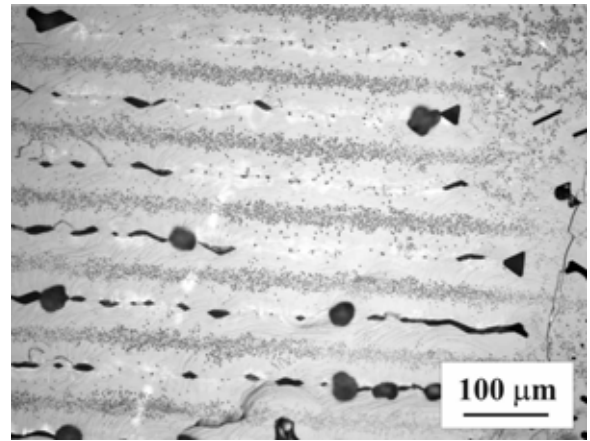


Fig. 9. Nomarski micrograph differential interference contrast (DIC) of GaN grown on a substrate with gallium nitride between stripes after defect-selective etching. Defect density in the laterally overgrown material was as low as $5 \times 10^5 \text{ cm}^{-2}$.

solution was constant i.e. the crystallization temperature decreased with increasing supercooling.

The increase of the temperature of crystallization results in a significant increase of the growth rate. We have shown this recently, for crystallization on a GaN substrate in a configuration identical to the one used for the construction of the diagrams presented (Fig. 7b). With a supercooling of 50 $^{\circ}\text{C}$ the growth on the GaN substrate at temperature range of 1430-1480 $^{\circ}\text{C}$ was more than twice faster than at a temperature range of 1400-1450 $^{\circ}\text{C}$ (Fig. 8b). It is therefore expected that a further increase of the growth temperature would allow us to achieve 5-10 $\mu\text{m/h}$. and to grow mm thickness GaN platelets.

Due to a very uniform crystallization front achieved in the high pressure solution growth of GaN on GaN/sapphire substrates, the ELOG type growth became possible (for details see [37]). The substrates were 4 or 8 μm thick GaN MOCVD layers (on sapphire) patterned by photolithography and reactive ion etching. The patterns were 20 μm wide and 3-4 μm high stripes arranged along $\langle 10\bar{1}0 \rangle$ or $\langle 11\bar{2}0 \rangle$ directions. The distance between the stripes was 300 or 60 μm . Depending on the initial GaN layer thickness, the surface between the stripes was sapphire or GaN. The high pressure crystallization processes were carried out at a N_2 pressure of 10 kbar, a temperature range of 1400-1450 $^{\circ}\text{C}$, in a vertical configuration, during 1 to 8 hours.

In most of the experiments, the initial stripes increased their width by about three times i.e. the laterally grown material extended by about 20 μm per side for both orientations used. Dislocation densities in the areas corresponding to the initial stripes were in the range of 10^7 - 10^8 cm^{-2} , that is close or slightly lower than in the initial MOCVD material. The dislocation densities in the material being the result of the lateral growth of the stripes were in the range of 10^5 - 10^6 cm^{-2} that is 2 to 3 orders of magnitude lower than in the

initial GaN. Figure 9 shows the surface of GaN after the ELOG-type growth and defect-selective etching indicating a much lower dislocation density in the laterally-overgrown material. A further step in this approach will be an appropriate masking of the substrate between the stripes to avoid coupling of the new grown material to the high dislocation density initial substrate.

HVPE of GaN on the pressure grown substrates

As mentioned in the Introduction, Hydride Vapor Phase Epitaxy is extremely efficient in a development of quasi bulk GaN technology. The method allows one to grow high purity GaN with rates of the order of 100 $\mu\text{m/h}$ which gives layers thick enough to separate them from the foreign substrates usually applied for deposition of III-group metal nitrides. On the other hand, the HVPE method has some limitations the main one of which is parasitic deposition of GaN occurring out of the substrate, leading to significant changes of growth conditions during the process. This is one of the reasons that despite the availability of the free standing GaN wafers, large bulk GaN single crystals are very difficult to grow by HVPE in a stable way.

The method was (and still is) also applied for the deposition of thick GaN on the pressure grown substrates [38, 39]. The HVPE system used for this purpose is a horizontal home-built quartz reactor with a rotating quartz susceptor. At present for most of the experiments, the configuration where GaCl is supplied vertically, just over the surface of the susceptor is being used. The conditions for this kind of the processes were: a growth temperature of 1030-1050 $^{\circ}\text{C}$, a temperature of GaCl synthesis of 800-850 $^{\circ}\text{C}$, HCl flow in the range of 4-24 mls/minute diluted in 200 mls/minute of N_2 , NH_3 in the range of 400-1200 mls/minute and 3000 mls/minute of N_2 as a carrier gas were applied for runs of 1 to 10h. The growth rates observed for this geometry and conditions varied from 30 to $>500 \mu\text{m/h}$. This was dependent on the HCl flow, on the details of the gas distribution in the system and on the arrange-

ment of the crystals on the susceptor. Even for the fastest growth (exceeding 500 $\mu\text{m/h}$.) the crystallization front was stable in terms of its flatness and the continuity of the new grown material-example in Fig. 10a. However, the morphology of the HVPE grown crystals improved with a decrease in the growth rate (Fig. 10b and c) becoming really good at a growth rate of about 100 $\mu\text{m/h}$ -Fig. 10c. Such a growth can be continued in a stable way, if parasitic deposition and gas flow perturbations due to the increasing height of the crystal are sufficiently suppressed.

The most typical macroscopic defects in the morphology of the fast grown crystals are large "pinholes" visible also on the surface of the samples shown in Fig. 10. It was shown [39] that their generation is related to the non-coherent inclusions of GaN observed especially in the crystals grown at very high rates.

The dislocation density in the thick GaN crystals grown by HVPE on the n-type GaN substrates determined by defect-selective etching (DSE) in molten KOH-NaOH eutectics, is 10^4 - 10^5 cm^{-2} . There are also low angle grain boundaries arranged along $\langle 10\bar{1}0 \rangle$ directions. The analysis of the DSE results [39] suggested the presence and the relaxation of strains typical for the systems with a small lattice mismatch. However, there are also data [39] showing that the generation of defects (at least part of them) in the HVPE GaN can be related to the still non-optimized conditions of the HVPE process. In particular, DSE showed the presence of dislocations arranged in hexagonal star-like patterns around the "pinholes. The patterns were similar to the ones generated in the pressure-grown GaN indented with a diamond [40]. The formation of the "pinholes and thus also an important number of dislocations, can be suppressed by lowering the growth rate and further optimization of the geometry of the HVPE system.

Applications of GaN grown by HVPE on the pressure grown substrates

It is expected that the application of epitaxial GaN-based quantum structures with non-polar orientations

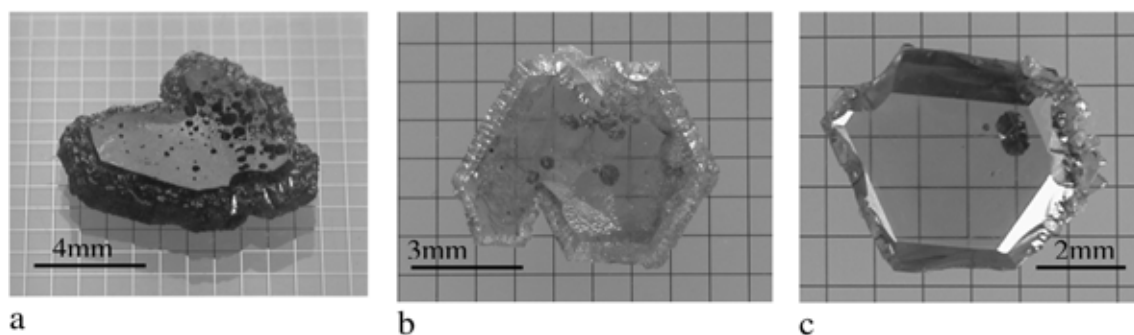


Fig. 10. GaN crystals grown by HVPE on pressure grown n-type GaN substrates. Rate of the growth: a-about 500 $\mu\text{m/h}$, b-about 250 $\mu\text{m/h}$, c-about 100 $\mu\text{m/h}$.

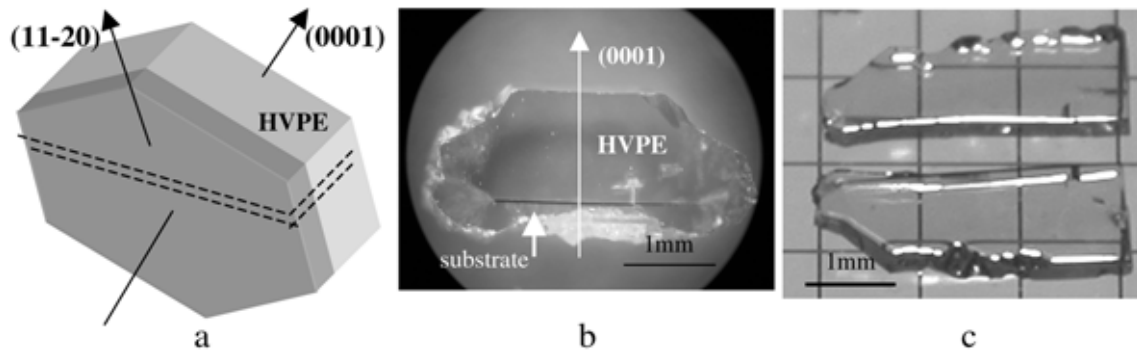


Fig. 11. Slicing of the “thick” GaN crystal along $\{11\bar{2}0\}$ non-polar crystallographic plane: a-schematic view, b-section across the crystal deposited by HVPE on the n-type pressure grown about 60 μm thick GaN substrate (visible as thin dark stripe), c-300 μm thick platelets with $\{11\bar{2}0\}$ surfaces polished.

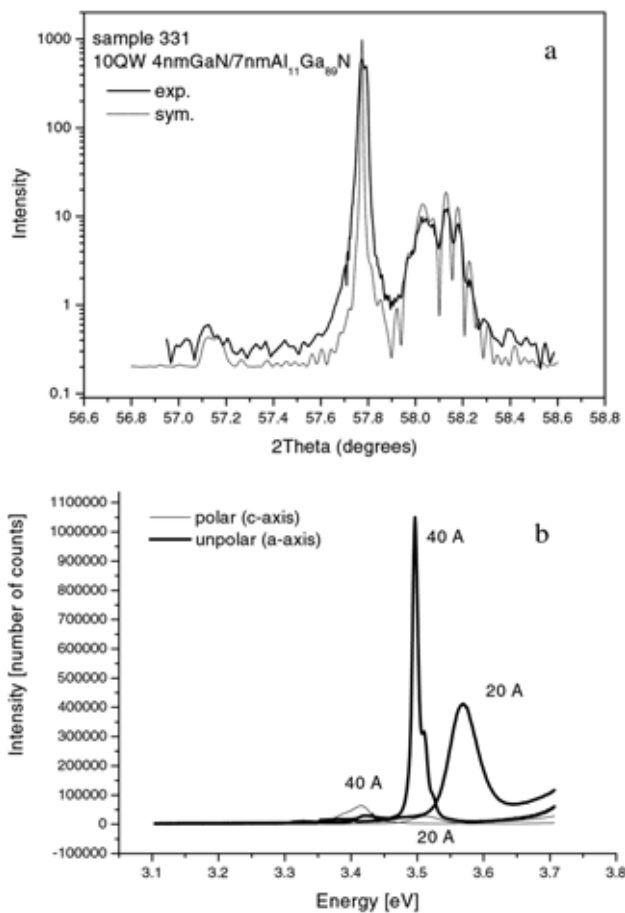


Fig. 12. GaN/AlGaIn MQW grown on non-polar GaN bulk substrates: a-XRD spectrum of one of the structures, b-low temperature (10K) photoluminescence spectra of 2 and 4 nm wide GaN/AlGaIn MQW grown by MBE on both non-polar $\{11\bar{2}0\}$ and polar (0001) GaN bulk substrates.

will lead to a significant increase of radiative process efficiencies due to the elimination of the built-in piezoelectric fields. To grow such structures, non-polar GaN bulk substrates were made by slicing the thick GaN crystals grown by HVPE on the pressure grown GaN substrates (Fig. 11). As can be noticed from this Figure, the sliced crystals are transparent, colorless,

without macroscopic defects like cracks, large inclusions or voids. The irregular shape of the platelets in Figure 11c is due to the large “pinholes”, apparently present on the (0001) surface of the initial crystal.

The 300 μm thick, $\{11\bar{2}0\}$ oriented slices were prepared for epitaxy by mechanical and chemical polishing. Then, 10-fold GaN/AlGaIn sequences of 2, 3, and 4 nm thick GaN quantum wells separated by 7 nm $\text{Al}_{0.11}\text{Ga}_{0.89}\text{N}$ barriers were deposited by plasma assisted MBE [41] on both the non-polar and the “usual” polar GaN substrates (for comparison of the optical properties). The structural quality of the “non-polar” MQW was good as shown by XRD measurements [41]. One of the corresponding spectra is shown in Fig. 12a.

According to expectations, much stronger UV emission was obtained from the “non-polar” multi quantum wells-Fig. 12b. The character of the low temperature photoluminescence spectra confirmed the high structural quality of these samples (for details see [41]).

Conclusions

In spite of their limited size, the GaN crystals grown from solution in gallium under a high N_2 pressure can be used as substrates for epitaxy and processed for making devices. Both highly conductive (n-type) and highly resistive (GaIn:Mg) substrates are available. Due to a very low threading dislocation density in the substrate material, the violet laser diodes with cleaved mirrors were fabricated by both MOCVD and plasma-assisted MBE (for the first time) on n-type crystals whereas the highest 2DEG mobility GaN/AlGaIn heterostructures were grown by MBE on the insulating crystals.

Increasing the size of the pressure-grown GaN crystals requires better control of the distribution of temperature and nitrogen concentration in the growth solutions with a large volume. The thickness of the crystals can be increased by directional crystallization on the (0001) surface of these crystals. A stable crystallization front was obtained for long duration

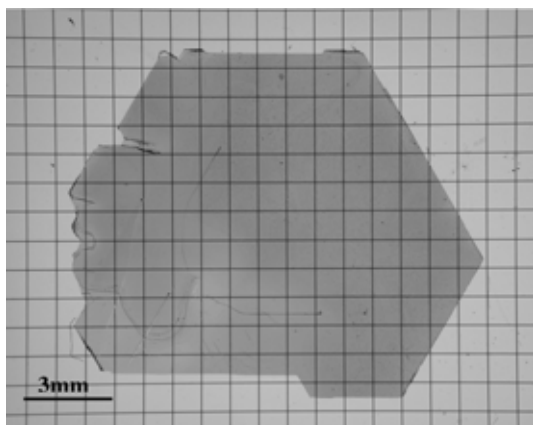


Fig. 13. One of the biggest GaN crystals grown from the solution in a temperature gradient without intentional seeding.

processes. The highest average growth rate observed up to now, for a 100 h process, on a GaN substrate, at a crystallization temperature of 1430 °C was as low as 1.8 $\mu\text{m/h}$. However it was more than twice faster that at 1400 °C under otherwise, identical conditions. It is expected then, that a further increase of the growth temperature and an improvement in the growth configuration would allow one to achieve 5-10 $\mu\text{m/h}$, which would be a reasonable rate to grow millimeter thickness GaN platelets. At present the solution growth of GaN crystals with larger lateral size seems even more challenging. The creation of a well defined, uniformly supersaturated crystallization zone in a large volume crucible is an obvious requirement to grow large crystals. The possibility to increase the size of the pressure-grown GaN platelets up to 15-25 mm is confirmed to some extent, by the results of crystallization on the free Ga surface (Fig. 4 and 5) and also by the spontaneous growth in a temperature gradient giving sometimes crystals larger than 10 mm (Fig. 13).

The thickness of the pressure-grown GaN crystals can be also increased by HVPE. The growth with a rate of about 100 $\mu\text{m/h}$ allowed us to increase the thickness of the substrate to about 2 mm resulting in crystals of excellent, stable morphology. The problem to solve is stopping the generation of dislocations in the thick HVPE GaN. This seems to be related to the small lattice mismatch between the substrates and the HVPE GaN but also, with the still non - optimized conditions of the growth.

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