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HIGH PRESSURE CRYSTALLIZATION OF III-V NITRIDES

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Crystal growth from the solution under high N_2 pressure (HNP method) results in high quality mm size crystals of GaN in 5 to 24 hour process. The crystallization of AlN is less efficient due to relatively lower solubility of nitrogen in the liquid Al. Possibility of InN growth is strongly limited since this compound is unstable at $T > 600^\circ\text{C}$ even at 20 kbar. The growth of cm size high quality GaN crystals requires lower supersaturations and longer processes.

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1. Introduction

Currently, the layers of III-V nitrides are grown on foreign substrates, mainly sapphire. Due to very high melting temperatures and/or pressures at melting, the substrate crystals of considered nitrides cannot be obtained by typical methods like Czochralski or Bridgman growth from the stoichiometric melts. Therefore, lower temperature methods, i.e. growth from the solution, have to be applied.

2. Thermal stability

The melting temperatures, T^M , and corresponding equilibrium pressures at melting, of III-N compounds were not measured. The melting temperatures were calculated by the use of Van Vechten's quantum dielectric theory of chemical bonding [1]. In Table I we have shown the calculated values of T^M and the estimations for corresponding pressures.

AlN, GaN and InN are tetrahedrally coordinated, strongly bonded compounds. The bonding energies are 2.88, 2.24 and 1.93 eV [5] for AlN, GaN and InN, respectively, whereas for i.e. GaAs it is 1.63 eV. The consequence of this are high melting temperatures, but also, good thermal stability of AlN and GaN. At N_2 pressure of 1 bar, AlN, GaN and InN are thermodynamically stable up to 2563 [6], 854 [7] and $\approx 400^\circ\text{C}$ [2] respectively. On the other hand, these temperatures are quite far from the expected melting points. Due to the strong triple bond

TABLE I

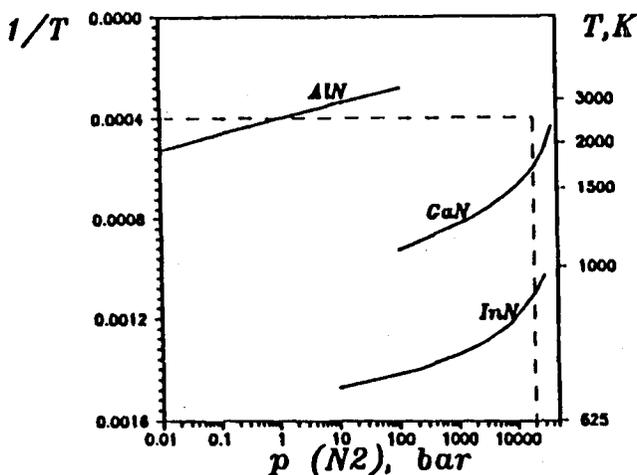
Melting conditions for AlN, GaN and InN.

Nitride	T^M [K]	Ref.	$p_{N_2}^*$ [kbar]	$p_{N_2,exp}^{**}$ [kbar]	Ref.
AlN	3487	[1]	0.2	> 0.1	[3]
GaN	2791	[1]	45	> 30	[4]
InN	2146	[2]	60	> 35	[2]

* Extrapolation of the experimental equilibrium data.

** The highest pressure at which the decomposition has been observed.

in N_2 molecule (9.76 eV), the pressure over InN and GaN reaches very high values, of several tenths of kbar, at temperatures approaching the melting points. For AlN, where nitrogen is bonded in the crystal very strongly, the pressure is not so high, however, at 2800°C, the decomposition pressure is higher than 100 bar [3]. In Fig. 1 we have shown the equilibrium curves for considered compounds.

Fig. 1. Equilibrium N_2 pressure over III-V nitrides: AlN [6], GaN [4], InN [2].

The equilibrium p - T curves for InN and GaN deviate from linear dependence due to nonideality of N_2 , accordingly, and the pressure is lowered in relation to that predicted for an ideal gas.

For our experimental system, where 20 kbar and 1800°C in reasonable volume (1–5 cm^3) is possible, each of the nitrides has its own experimental limitations.

For AlN, we have only the technical limit related to temperature since the pressure requirements can be assured even for melting.

For InN, we have the pressure limit of 20 kbar which determines the maximum temperature of InN stability. This is only 550–570°C which is very far from the expected melting point.

For GaN, the maximum equilibrium temperature determined by pressure of 20 kbar is 1600°C which is the closest to melting. This creates the best conditions for crystallization among the considered nitrides.

3. Liquidus curves

In Fig. 2 we have shown the experimental data of nitrogen solubility in liquid gallium [8]. At the temperature range of 1200–1600°C, the equilibrium content of N in the liquid increases by two orders of magnitude and reaches 10^{-2} at. fraction.

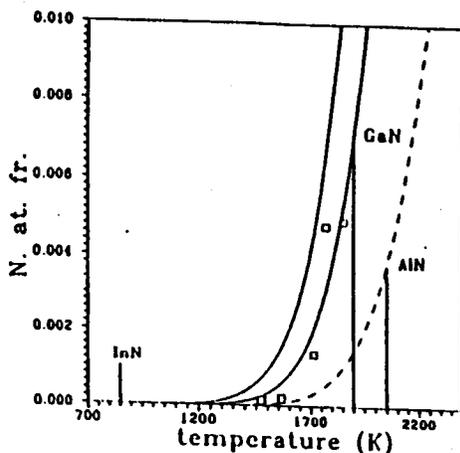


Fig. 2. Solubility of N in liquid Al, Ga, In.

The solubility curves for AlN, GaN and InN calculated in regular solution approximation are shown in Fig. 2. The data indicate that at the conditions available in gas pressure system, the highest solubility can be expected for GaN and the lowest for InN.

4. Synthesis and crystal growth

4.1. Experimental

Crystal growth experiments were performed in a gas pressure chambers of internal diameter 30 mm (the growth setup was presented in Ref. [9]) with a furnace of inside diameter 14 mm (1500°C) or 10 mm (1800°C) and with a BN crucible containing Al, Ga or In. The temperatures were stabilized with the precision better than 1°. Usually, the crystals were grown at a pressure for which the nitride was stable over the whole temperature range along the crucible.

4.2. Results — AlN and InN

At high N_2 pressure, the synthesis rate is very high for AlN and extremely low for InN. The rate of AlN synthesis is so high that, at pressure lower than 6.5 kbar, thermal explosion is observed during heating of the bulk Al sample (Fig. 3).

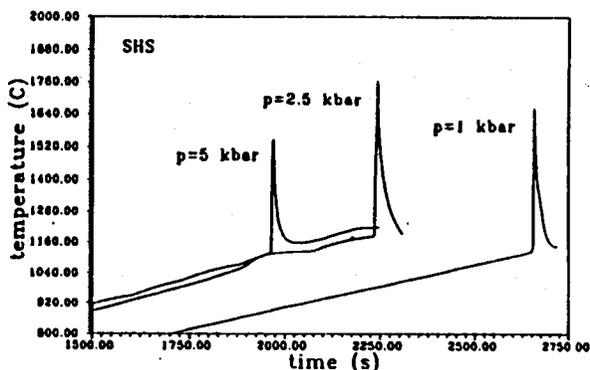


Fig. 3. Temperature of the Al sample during heating at a rate of $20^{\circ}/\text{min}$, at high N_2 pressure.

The combustion product is AlN powder or ceramics. At higher pressures, a tight AlN layer inhibits further reaction and the metal can be heated up to the temperature of crystallization.

Due to low solubility, the crystallization rate of AlN, at $1600\text{--}1800^{\circ}\text{C}$, is rather low ($< 0.02\text{ mm/h}$).

Due to kinetic (low temperature) and thermodynamical (low solubility) barriers crystal growth experiments for InN resulted in very small crystallites ($5\text{--}50\ \mu\text{m}$), grown by slow cooling of the system from the temperatures exceeding the stability limit for InN.

4.3. Results — GaN

GaN crystals were grown from the solution in liquid Ga, in quasilinear temperature gradient of $30\text{--}100^{\circ}/\text{cm}$, in 5–24 hour processes. The experiments were performed at N_2 pressure of 8–17 kbar, at temperatures of $1300\text{--}1600^{\circ}\text{C}$.

A typical synthesis solid diffusion (SSD) crystallization mechanism was observed. The synthesis of thin polycrystalline GaN film on the Ga surface, its dissolution and transport into the cooler part of the crucible lead to the nucleation and growth of GaN single crystals.

The morphology of the crystals depends on pressure, temperature range and supersaturation during growth. For pressures and temperatures lying deep in the GaN stability field (higher pressures, lower temperatures), the crystals are hexagonal prisms elongated in the c -direction. At the conditions close to the equilibrium curve, the dominating shape is a hexagonal plate.

The crystals which grow slowly (slower than 0.1 mm/h), i.e. at smaller temperature gradients, are of high structural quality. They are transparent, slightly yellowish, and have flat mirror-like surfaces. In Fig. 4a we have shown some of these crystals grown at $1400\text{--}1500^{\circ}\text{C}$, at 10 kbar in a 20 h process. Figure 4b is one of the scanning tunneling microscopy (STM) scans [13] of (0001) surface. STM measurements confirm that the surfaces of the crystals are flat, however, some steps $20\text{--}40\ \text{\AA}$ high were observed.

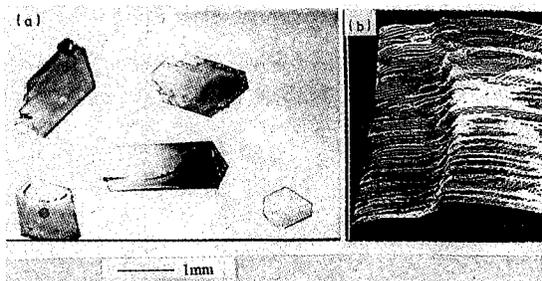


Fig. 4. (a) GaN single crystals grown at 10 kbar in 10 h, (b) STM scan indicating 40 Å step on GaN (0001) surface.

Typical widths (FWHM) of X-ray rocking curves for (004) Cu K_{α} reflection, are 23–32 arcsec. The FWHM determined in several points (typically 8) for the GaN platelets 2.5×2.5 mm scatters by ± 3 arcsec. The typical X-ray rocking curve for (0004) reflection, characterizing the crystals, is shown in Fig. 5a. The curve is significantly narrower than the curves of heteroepitaxial GaN layers grown by MOCVD (metalorganic chemical vapor deposition) or MBE (molecular beam epitaxy). This is illustrated in Fig. 5b.

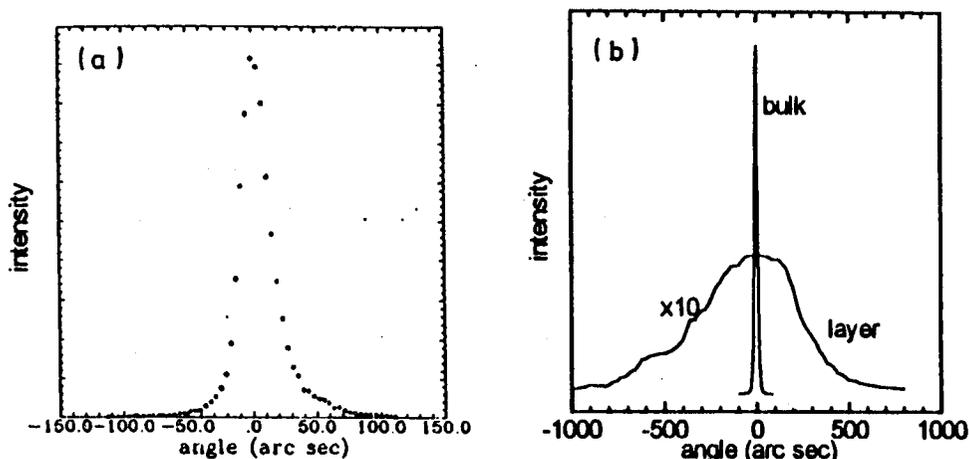


Fig. 5. (a) Rocking curve for GaN plate. (b) Rocking curves for crystal and heteroepitaxial layer grown by MOCVD on sapphire substrate [14].

A GaN 2 mm plate was used as a substrate for GaN homoepitaxial growth by HNP Ga vapor transport, in temperature gradient. A $5 \mu\text{m}$ GaN layer was obtained in 3 h process. The rocking curve of the layer was broadened, in relation to the substrate, up to 40–42 arcsec.

The quality of GaN crystals deteriorates with increasing growth rate (high supersaturations) and with dimension of the crystals. The latter is related to the

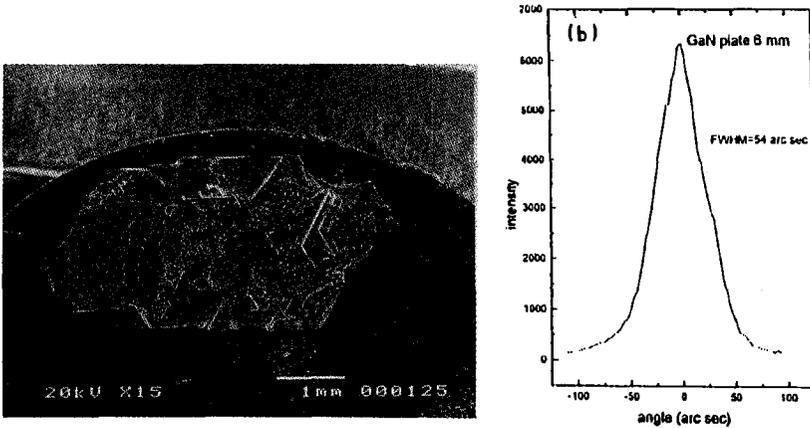


Fig. 6. (a) GaN plate grown at 1250–1400°C, at 12 kbar N_2 pressure during 8 h. (b) Rocking curve of the crystal from Fig. 6a measured with 1×3 mm X-ray beam.

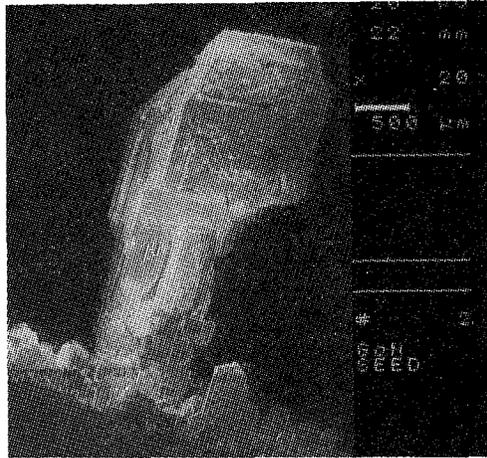


Fig. 7. Growth of GaN on GaN seed crystal.

non-uniform distribution of nitrogen in the solution across the growing crystal face, especially if the face reaches the size comparable with size of the crucible. In this case the layer-by-layer growth mechanism is strongly disturbed. This leads to the formation of macrosteps on the crystal surfaces and acceleration of the growth near the edges of the crystals. In extreme, for the growth rates above 1 mm/h, the formation of unstable: hollow, skeletal or dendritic crystals is observed.

The deterioration of quality of the 5–10 mm crystals grown at the rate of 0.5–1 mm/h is reflected in the broadening of the rocking curve. Figure 6 shows 6 mm GaN plate and its rocking curve. The FWHM of the curve is 50 arcsec. In some cases, the splitting of the reflection curve into two or three peaks is observed

TABLE II

Physical properties of GaN crystals grown under high N₂ pressure.

Property	Value	Method
Lattice constants	$a = 3.1879\text{--}3.1895 \pm 0.0004 \text{ \AA}$ $c = 5.1856\text{--}5.1863 \pm 0.0002 \text{ \AA}$	Bond
Size	up to $2.5 \times 2.5 \times 0.2 \text{ mm}$	
Rocking curve (0004), Cu K α	23–32 arcsec	
Surface (0001), as grown	flat	SEM
	steps 20–40 \AA	STM
Impurity content	< 0.1%	EDX
Electron concentration	$\approx 10^{19} \text{ cm}^{-3}$	optical, Hall effect
Mobility	$\approx 100 \text{ cm}^2/(\text{V s})$	el. conductivity
$E_g + E_F$, at 20 K	3.55–3.58 eV	optical absorption
Pressure coeff. of E_g	4.7 meV/kbar	opt. abs. in DAC
Refractive index at 1.7 eV	2.43	
Photoluminescence on Zn at room temp.	2.85 eV	
Bulk modulus	2450 kbar	EXAFS
Thermal expansion coeff.	$\alpha_{a(294 \text{ K})} = 3.1 \times 10^{-6} \text{ K}^{-1}$ $\alpha_{c(294 \text{ K})} = 2.8 \times 10^{-6} \text{ K}^{-1}$ $\alpha_{a(700 \text{ K})} = 6.2 \times 10^{-6} \text{ K}^{-1}$ $\alpha_{c(700 \text{ K})} = 6.1 \times 10^{-6} \text{ K}^{-1}$	X-ray
Phonon energies	$A_1(\text{TO}) = 530 \text{ cm}^{-1}$ $E_1(\text{TO}) = 560 \text{ cm}^{-1}$ $E_2(\text{high}) = 568 \text{ cm}^{-1}$ $E_2(\text{low}) = 144 \text{ cm}^{-1}$	Raman scattering
GaN plate		
Size	5–10 mm	
Rocking curve	48–54 arcsec	
Surface (0001), as grown	macrosteps 1–3 μm	SEM, STM
Homoepitaxial layer on GaN 2 \times 2 mm substrate		
Rocking curve substrate	25–30 arcsec	
layer	38–42 arcsec	

which indicates the presence of low angle (1–2 arcmin) boundaries in the cm size GaN crystals.

Attempts to grow GaN on single crystalline GaN seed were also undertaken. Figure 7 shows a GaN crystal grown on $0.4 \times 1.6 \text{ mm}$ needle shaped GaN seed, in

vertical crucible, in 8 h process. The use of seed hindered the growth of GaN crystals on the crucible walls. Layer growth on the seed faces was observed, however, patterns characteristic of unstable growth (edge nucleation, accelerated growth near edges and macrosteps) were also visible.

Physical properties of the crystals were determined by X-ray [10], electrical and optical [11] measurements. Pressure dependences of energy gap [11] and phonon energies [12] were measured. Table II contains the fundamental physical properties of pressure grown GaN crystals.

5. Conclusions

High quality crystals of III-N compounds can be grown at nitrogen pressure up to 20 kbar. At this pressure range, the best results were obtained for GaN. AlN requires higher temperatures to increase the solubility of N in the liquid Al. For InN, the pressure of 20 kbar is not sufficient for effective crystallization.

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