Journal of Crystal Growth 312 (2010) 2593–2598

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

The influence of indium on the growth of GaN from solution under high pressure

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ARTICLE INFO

Available online 21 April 2010

Keywords:
A2. High pressure growth from solution
A2. Single crystal growth
B1. Gallium nitride

ABSTRACT

The influence of significant fraction (10–50 mole%) indium in liquid gallium on GaN crystallization from a ternary Ga–In–N solution was analyzed. Crystallization experiments of GaN on GaN-sapphire templates from Ga–In solutions, at 1350–1450 °C, with prior to the growth seed wetting at 1500 °C, and 1.0 GPa N_2 pressure, without solid GaN source showed faster growth of GaN on the seed (by a factor of 1.5–2) than using pure gallium solvent. Nevertheless the new grown crystals were morphologically unstable. The instability was reduced by decrease of the wetting temperature down to 1100 °C or by omitting the wetting procedure entirely, which indicated that GaN dissolves much faster in Ga–In melt than in pure Ga and that the unstable growth was caused most likely by complete dissolution of GaN template before the growth. It was observed that the crystals grown on bulk GaN substrates did not show morphological instability observed for GaN-sapphire templates. The influence of indium on thermodynamic and thermal properties of the investigated system is discussed.

1. Introduction

At present, stringent efforts are undertaken to develop crystallization methods of large size, high quality GaN bulk crystals. However the final goal: perfect, large and commonly available GaN crystals is still a challenge because of extreme congruent melting conditions of this compound (2220 °C, 6 GPa) [1], making application of the melt growth techniques technically impossible. The methods, allowing use of significantly lower temperatures and pressures than these required for melting have their specific limitations, of which the most important is low rate of crystallization, especially for ammonothermal and solution growth systems.

The high nitrogen pressure solution (HNPS) growth is one of the few methods giving single crystalline GaN which is successfully used for fabrication of laser diodes [2]. This is possible due to extremely low dislocation density and very high, uniform electrical conductivity of this material. In the GaN crystals, grown by the HNPS method without intentional seeding [3], threading dislocation densities (TDD), measured by defect selective etching of (0 0 0 1) Ga-polar surfaces, are lower than $100\,cm^{-2}$. The crystals are heavily n-type (about $5\times10^{19}\,cm^{-3}$) unintentionally doped by oxygen, making them strongly and uniformly conducting. The free electrons can be removed by compensation with magnesium acceptor added to the growth solution and, in this way, semi-insulating GaN can be grown. Due to relatively low equilibrium concentration of nitrogen in the liquid gallium at the growth temperatures of 1400–1500 °C (0.1–0.3 mol% respectively) the maximum rate of stable crystallization is fairly low. For thin platelets, it is about 1 μm/h for ⟨0 0 0 1⟩ direction and about 100 μm/h for lateral directions.

The problem of limited size of spontaneously grown high pressure GaN crystals is being solved by the use of seed crystals grown by HVPE [4]. In this way the 1–2 in (0 0 0 1) oriented pressure grown substrates, with dislocation density significantly lower than in the seed, can be obtained. The crystals are grown on one surface of the seed (horizontal configuration) or on two opposite surfaces for seeds immersed in the solution (vertical configuration). Afterwards the seeds are removed from pressure grown crystals by sawing or polishing to obtain free standing, highly conducting GaN.

In the horizontal configuration, the seed crystal is placed at the bottom or at the top of the crucible, filled with liquid gallium. Temperature gradient is applied along the axis of the crucible. Typical temperature range is 1400–1500 °C at 1.0 GPa N_2 pressure. In Fig. 1, the horizontal configuration is schematically shown. Crucibles with internal diameter of 18, 25 and 50 mm are used for crystallization on various substrates, including HNPS GaN crystals (small, TDD $<100\,cm^{-2}$), HVPE GaN crystals (TDD $=10^6$–$10^7\,cm^{-2}$) and MOVPE GaN-on-sapphire templates (TDD $=10^8$–$10^9\,cm^{-2}$).

The crystals grown by the HNPS method on the substrates are usually macroscopically flat with macroscopic growth steps covering the growth surface—Fig. 2a–c. The formation of these

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doi:10.1016/j.jcrysgro.2010.04.018

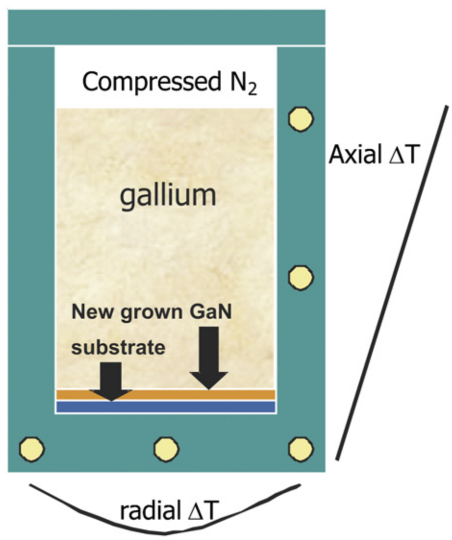

Fig. 1. Horizontal configuration used for seeded HNPS growth of GaN: crucible with typical temperature distribution in the crucible wall and in the crucible bottom.

growth features is a sign of non-uniform supersaturation across the growing surface.

In this work, the possible influence of indium, added to the gallium solvent in significant fraction (10–50%), on seeded GaN crystallization in horizontal configuration was investigated. The following aspects were taken into account:

1. Possible increase of equilibrium solubility of GaN in the liquid metal by dilution of gallium with indium due to decrease of the chemical potential of Ga in the liquid phase.
2. Corresponding adjustment (increase) of activity of N_2 gas, necessary for the solvent in contact with the gas.
3. Possible changes in temperature distribution due to different physical properties of indium and gallium metals.
4. Higher potential barrier for dissociation of N_2 molecule for gallium partially replaced by indium: it should result in reduced parasitic crystallization rates but also in slowing down of nitrogen dissolution in the metal (from gaseous source of nitrogen).

2. Experimental procedures and results

Basic experimental configuration used for this study was the one shown schematically in Fig. 1. The 3 μm thick GaN-on-sapphire substrates grown by MOVPE were placed on the bottom of the graphite crucible, filled with gallium and indium mixture. Prior to the growth, the system was overheated above GaN–Ga–N2 equilibrium conditions to assure a good wetting of the substrate with liquid metal. The first experiment was carried out at the following conditions:

Procedure 1

Substrate: GaN-on-sapphire, (0 0 0 1)
Solvent: 50 mol% Ga+50 mol% In
Wetting: 1500 °C, 2 min
Axial ΔT: 1350–1450 °C measured in crucible wall along 15 mm high metal sample
Radial ΔT: 1300–1350 °C measured along 10 mm radius of the crucible bottom

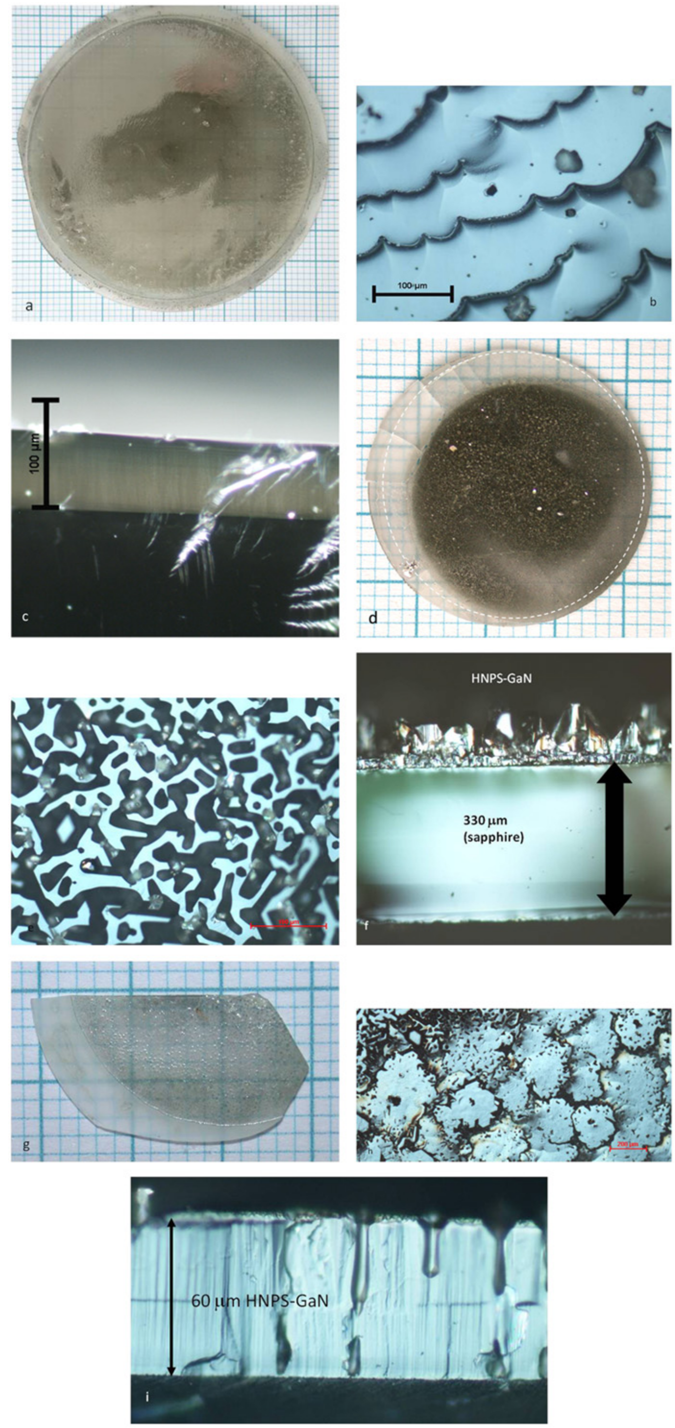

Fig. 2. GaN crystals, grown on GaN sapphire substrates, at the conditions specified in the text: a,b,c — general view, surface morphology and cross section, respectively, of the crystal grown from solution in pure gallium in 80 h process with high temperature wetting of the template, d, e, f—general view, surface morphology and cross section, respectively, of the crystal grown from solution in 50 mol% Ga+50 mol% In with high temperature wetting of the template, g, h, I — the same as "d, e, f" but with low temperature wetting. In "a, d g" the distance between grid lines is 1 mm.

N_2 pressure: 10 kbar
Duration: 25 h.

The reference experiments with pure gallium solvent and at otherwise, identical conditions [3], resulted in transparent, newly grown GaN crystals (layers) with macroscopically flat surfaces,