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Growth and characterization of GaN single crystals

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Abstract

Up to 3 mm long GaN single crystals were grown by sublimation of cold pressed GaN pellets or evaporation of gallium (Ga) metal under an ammonia (NH_3) flow in a dual heater, high-temperature growth system. A growth rate of 500 μm/h along the [0 0 0 1] direction was achieved using a source temperature of 1200°C, a total pressure of 760 Torr, and an NH_3 flow rate of 50 sccm. The resulting crystals were transparent, possessed low aspect ratios and well-defined growth facets. The only impurity present at high concentrations was oxygen (3×10^{18} atoms/cm^3). Photoluminescence studies conducted at 77 K showed a sharp emission peak centered at 359 nm. Time-dependent photoluminescence measurements revealed optical metastability in bulk GaN. Raman spectroscopy yielded narrow peaks representing only the modes allowed for the wurtzite structure. All characterization studies confirmed excellent crystalline and optical quality of the obtained single crystals. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The achievement of blue and green light emitting diodes and blue emitting lasers [1], as well as prototypes of several microelectronic devices produced from GaN-based materials is intriguing, given the high density ($\geqslant 10^9$ cm^{-2}) of dislocations present in most device structures. Substantial defect reduction via the use of lateral overgrowth techniques and substrate removal have resulted in reported lifetime assessments of 10,000 h for the blue laser diodes [2]. This has had a significant impact on the commercial importance of this material [3]. However, the increased number of process steps leading to defect reduction increases the fabrication costs of devices. The availability of low defect density GaN substrates on which homoepitaxial films can be grown should result in marked improvements in device performance at reduced cost.

Growth of the GaN bulk crystals is a challenge due to its high melting temperature, low sublimation/decomposition temperature relative to its

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melting temperature, very high equilibrium nitrogen vapor pressure at moderate temperatures, and low solubility in acids, bases and most other inorganic elements and compounds. Novel bulk growth techniques must be employed which either take advantage of these inherent properties or surmount the difficulties presented by them.

Elwell and Elwell [4] reviewed the bulk GaN crystal growth research in 1988. The two most widely investigated approaches to date have been solution growth [5–10] and vapor phase transport [11–15]. The success of these methods has been limited to small crystals. The use of high-pressure solution synthesis has resulted in increasingly larger crystals. The initial research [13,14] with this last technique produced thin platelets limited in size to ≈ 1 mm. Recent research by these authors has resulted in crystals 8 mm square × 0.2 mm thick grown at a rate along the *c*-axis of $\approx 20\ \mu$m/h [10]. As reported, crystal quality decreased with increasing platelet size. Homoepitaxial thin film growth on good sections of these crystals resulted in a marked improvement in defect reduction relative to the films grown on foreign substrates.

Vapor phase transport has been employed by Sakai and co-workers [16] for the growth of GaN needles on sapphire substrates via sublimation of GaN powder in a flow of NH_3. The average crystal size was reported to be a few hundred micrometers. Homoepitaxial film growth by these investigators also resulted in decreased defect densities relative to films grown on foreign substrates. The above results indicated that bulk crystal growth of GaN can be achieved; however, the parameters necessary to enhance the size and quality of the crystals are rather precise and must be closely controlled.

The research described in the following sections deals with GaN crystal growth from the vapor phase via evaporation of Ga metal or sublimation of GaN powder in an NH_3 environment at temperatures higher than reported previously. Comparisons of optical microscopy, photoluminescence (PL), Raman spectroscopy, and secondary ion mass spectroscopy (SIMS) results with those available in the literature indicate that crystals grown in this research by this technique are of excellent quality.

2. Experimental procedures

2.1. Consolidation of gallium nitride powder

Consolidated GaN powder was selected as one of the source materials for the crystal growth experiments. Compact shapes are easier to contain during sublimation at low pressures and provide flexibility in positioning the source material.

Gallium nitride begins to decompose above 800°C under one atmosphere of nitrogen [17]. The melting point of GaN is not known; however, most theoretical estimates place it above 2000°C. Bulk diffusion, sufficient to achieve densification in refractory materials, is usually achieved at approximately two-thirds of their respective melting points; therefore, densification via sintering was impossible, even with small grain size material. Hot and cold isostatic pressing were deemed the most feasible methods for densification of this material.

Compacting GaN powder via the first method was unsatisfactory. High-purity GaN powder produced in our laboratory [18] was successfully compacted into pellets via cold isostatic pressing. This powder possessed exceptional structural quality and has been classified as the new X-ray standard (* quality) for this material [19]. The powder was subsequently jet milled (Model 00 Jet-O-Mizer grinding system at Fluid Energy Aljet Inc, PA) in an N_2 ambient. The feed rate and manifold pressure were 75 g/h and 7 kg/cm^2, respectively. Reduced particle size and improved particle uniformity were obtained which enhanced the cold pressing results.

Cylindrical pellets, 13 mm diameter and 6 mm in height, were prepared in stainless steel dies using an uniaxial cold press at pressures between 1575 and 2200 kg/cm^2. Delamination of the pellets was observed above 1750 kg/cm^2. The pressure range of 1650–1700 kg/cm^2 was optimum. Pellets used for the crystal growth experiments were pressed at 1700 kg/cm^2. Approximate green densities ranged from 60% to 70% of theoretical. Firing the GaN pellets in N_2 atmosphere at 700°C resulted in a negligible increase in density.

2.2. Crystal growth

Crystal growth of GaN was achieved by subliming cold pressed pellets of GaN in a stream of 99.9999% pure NH_3 gas. An alternative route of crystal synthesis employed the evaporation of 99.999% pure elemental Ga in the same purity of NH_3. All experiments were conducted in a dedicated system, specifically designed for GaN crystal growth. The reaction tube was isolated from the heaters and contained the source and seed materials. Two independently controlled heaters were used to achieve the temperature gradient necessary for growth. The growth system is shown schematically in Fig. 1.

The source and seed holder assemblies were manufactured from hot pressed boron nitride (BN) having an open porosity of 9%. The BN was chosen due to its ease of machining and inertness to NH_3. Blank BN seed holders served as the primary nucleation surfaces; however, 6H–SiC (0 0 0 1) seed crystals were used in a limited number of experiments. A source-to-seed distance of ~ 25 mm was employed in all experiments. The experimental arrangement allowed NH_3 to flow from the top.

All growth experiments were performed within the range of 1100–1450°C at the source heater and 1200°C at the seed heater. Growth pressures of 50–760 Torr were investigated; however, most experiments were conducted at 600 Torr. An NH_3 flow rate of 50 sccm was used for all experiments.

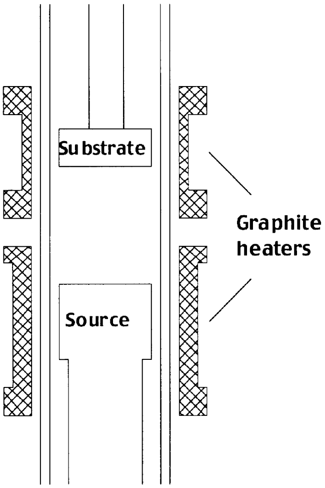

Fig. 1. Schematic of the dual heater system used to grow GaN crystals.

2.3. Characterization

The presence and concentrations of impurities in the GaN crystals were determined using a Cameca SIMS employing a 10 keV O_2^+ primary ion beam rastered over a 100 μm² area. The O_2^+ current was varied from 10 to 100 nA to obtain optimum secondary ion signal levels. The sample was biased at 4500 V, and the presence of H, C, O, Si and Ga (matrix reference signal) was investigated. Impurity concentrations were quantified using standards consisting of the impurity of interest implanted into monocrystalline GaN films grown in this laboratory. Data were acquired from both the standard and the samples under identical instrumental conditions. A relative sensitivity factor (RSF) was then obtained from the standard utilizing a known implanted impurity dose. The sample data were quantified by first taking the ratio of the intensity of the impurity of interest to the matrix reference signal and multiplying the result by the RSF.

Micro-Raman spectra of the GaN crystals were obtained at room temperature using a back scattering geometry from the [0 0 0 1] face and the 514.5 nm line of an Ar-ion laser. The spot size and the spectral resolution were 4 μm and 2 cm^{-1}, respectively.

The PL studies employed a frequency tripled, mode-locked, femtosecond (fs), titanium : sapphire laser. The duration of the excitation pulses was ≈ 250 fs. The emitted light was collected, collimated, and focused onto the entrance slits of a 0.32 m spectrometer. The signal was detected using a cooled gallium arsenide array detector. The PL studies were performed on the crystals pressed into indium metal bonded to a copper plug. The samples were oriented with their *a*-axis perpendicular to the laser beam.

A Cary 5 absorption spectrophotometer was used for the optical absorption studies. An ultraviolet grade optical fiber suitable for the sample size was used to project the light from the monochromator onto the sample. This was necessary, since any light not collected by the detector due to scattering or other phenomena would appear in the data as being absorbed. An S-20 photomultiplier tube (pmt), sensitive to ultraviolet light, was used to collect the light transmitted through the sample. A lock-in amplifier or an electrometer was used to detect the signal. Each scan was baseline corrected. The transmission curves were normalized to 650 nm, where the samples were known to be essentially transparent, and adjusted for the dark current of the pmt above the band gap.

3. Results and discussion

Hexagonal single crystals of colorless GaN up to 3 mm in length were grown by spontaneous nucleation on hot pressed BN surfaces from either cold pressed GaN pellets or Ga metal in a stream of ammonia. Fig. 2 shows an optical micrograph of ≈ 1 mm long, well faceted, transparent GaN crystals with low aspect ratios. The shape of these crystals is in great contrast to the needle-shaped crystals grown via vapor phase reaction by other authors. The growth time, pressure, and temperature of the BN surface used for the growth of these crystals were 2.5 h, 600 Torr, and 1000°C, respectively.

The majority of the experiments using the GaN pellets were conducted at a source temperature of 1200°C; above this temperature and under an NH_3 flow rate of 50 sccm, the GaN source began to convert to Ga metal. After each run, the pellets appeared darker in color due to nitrogen loss and small metallic Ga droplets were observed on the surface which became larger (millimeter size) in prolonged runs. Increasing the growth time beyond 2–3 h yielded GaN crystals that ranged from amber to gray in color, indicative of nonstoichiometric concentrations of nitrogen in the lattice. This is believed to be caused by the combination of a changing crystal surface temperature and an insufficient N incorporation. As the crystals grew, the temperature at the growth surface very likely decreased leading to lesser N incorporation and reduced growth rates. The temperature drift within the growth cavity was probably due to changing surface emissivity as more material was deposited on the inner walls of the crucible. Such changes would affect the kinetics of the NH_3 decomposition, as well as the source material surface temperature. It is, therefore, essential to control the growth in such a way that it occurs only at one selected growth site.

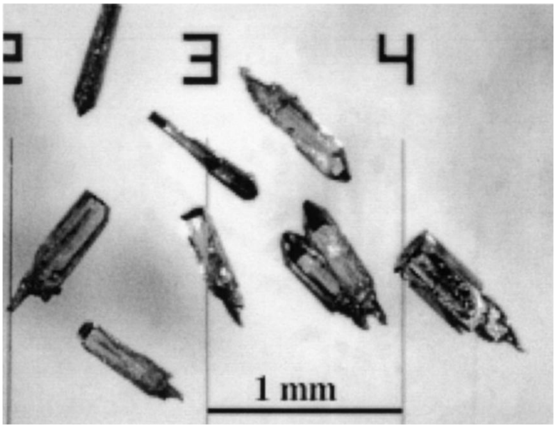

Fig. 2. Optical micrograph of selected GaN crystals with low aspect ratios.

When metallic gallium was used as a source material, source temperature had to be reduced to prevent oversupply of Ga, since the vapor pressure of Ga over its melt is much higher than that over GaN. In addition, Ga reacts vigorously with ammonia in the temperature range from 950°C to 1100°C, resulting in powder formation and coverage of the entire interior of the growth assembly. This reaction can be avoided if the system is held above this temperature range. Due to the above two constraints, the temperature of the Ga source had to be controlled in a relatively narrow range. In these experiments, the temperature was not high enough to prevent the formation of a thin skin of GaN on the surface of the molten Ga. The formation of this layer likely reduced the Ga flux, as increased growth times using metallic Ga as a source did not yield larger crystals. Experiments to establish the conditions under which the thickness of this skin and the supply of Ga can be maintained constant during a run are under way.

The direction of the fastest growth and, thus, the crystal morphology were observed to change with the changing Ga/NH_3 flux ratio and the growth temperature regardless of the Ga source. This was

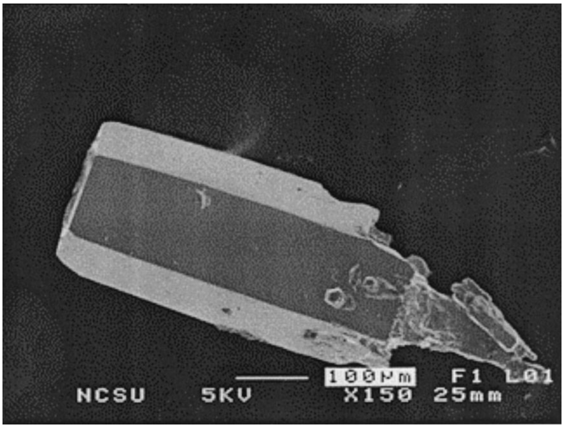

Fig. 3. SEM image of a 1 mm long GaN crystal with a low aspect ratio showing well-developed $(1\,0\,\bar{1}\,0)$ and (0 0 0 1) crystallographic facets.

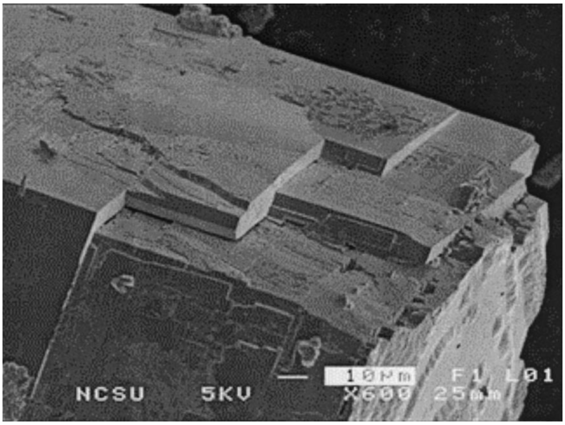

Fig. 4. High magnification of the crystal from Fig. 3 showing the growth habits on (0 0 0 1) and $(1\,0\,\bar{1}\,0)$ planes.

a significant observation in that all previous reports indicated that the growth of bulk GaN from the vapor phase resulted primarily in long needles. The aspect ratio of GaN crystals decreased with increasing Ga/NH_3 ratio. Growth at high Ga/NH_3 ratios resulted in the formation of a mixture of GaN powder and plate-like crystals, which were darker in color in comparison to those grown at a lower Ga/NH_3 ratio. The latter were transparent and needle-like in morphology. It is difficult to assess the independent effect of temperature on crystal morphology in the present system, since the decomposition kinetics of NH_3 changes with temperature. However, it can be stated that the needle-like crystals were grown at a relatively cooler site in the system. Figs. 3 and 4 show SEM images of a crystal which grew from a single isolated nucleation site (the bottom right corner of Fig. 3) and developed into a well-faceted hexagonal shape terminated by flat $(1\,0\,\bar{1}\,0)$ and (0 0 0 1) planes.

An SIMS scan indicated that all impurities with the exception of oxygen were at background levels. The quantitative results for C, H, O and Si are presented in Table 1. These impurity levels are similar to those detected in the CVD-grown high-quality GaN thin films [20]. Oxygen incorporation can likely be further minimized by using a higher grade of NH_3.

Table 1
Results of the SIMS analysis of the grown GaN crystals

Element	Concentration (atoms/cm^3)
C	2×10^{16}
H	5×10^{16}
Si	1×10^{16}
O	3×10^{18}

A representative PL spectrum for bulk GaN taken at 300 K is shown in Fig. 5. Strong bound exciton emission with a peak position at 365.0 nm (3.4 eV) and an FWHM of 9.0 nm (83 meV) was observed. The visible portion of the PL spectrum is expanded 500 times in the inset in Fig. 5. No yellow luminescence was detected. The spectrum obtained at 77 K had a peak positioned at 359.0 nm with an FWHM of 54 meV. A slight red shift, as compared to the results from the GaN thin films, is believed to arise due to the lack of stress in bulk crystals.

Data representative of the time-dependent photoluminescence obtained at 77 K in 5 min intervals are shown in Fig. 6(a)–(d). The first emission spectrum (Fig. 6(a)) corresponds to the band edge emission (peak wavelength = 359 nm, FWHM = 54 meV). After some time, a new emission band started emerging on the long wavelength shoulder of the original luminescence peak and the luminescence changed from invisible to blue. After the

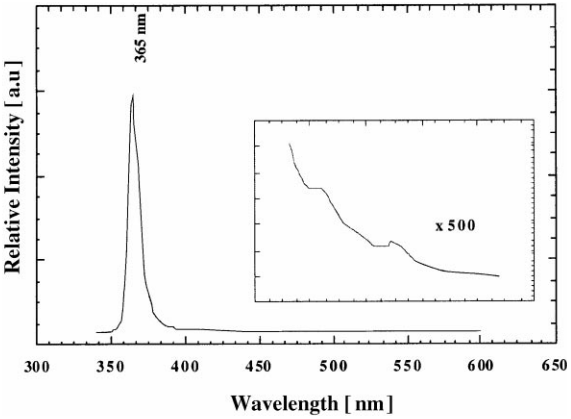

Fig. 5. Photoluminescence spectrum of bulk GaN taken at 300 K. Spectrum lacks yellow luminescence characteristic of defective GaN.

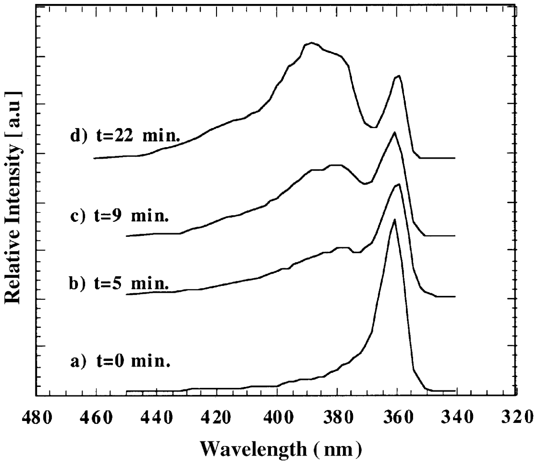

Fig. 6. Time-dependent photoluminescence spectrum of bulk GaN taken at 77 K. The low-energy peak became progressively more intense with the illumination time.

sample had been exposed to the pump-light for 22 min (spectrum 6d), the photo-induced emission band was centered at 388 nm and included LO-phonon replicas with zero-phonon peak centered at 378 nm. The energy separation between the phonon peaks was about 85 meV, which is close to the reported value of 90 meV for the LO-phonons in wGaN [21]. The FWHM of the blue emission was 249 meV. The significant spectral width of the phonon-assisted recombination implies a strong lattice interaction.

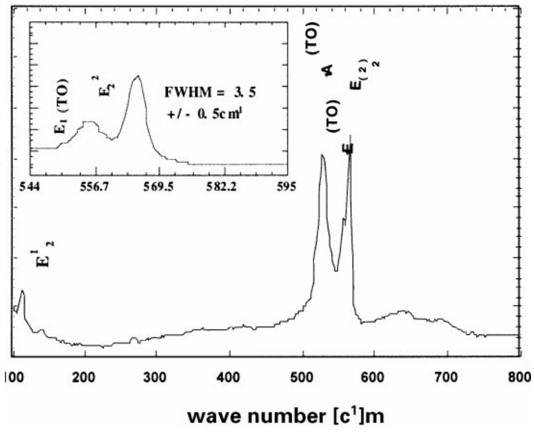

Fig. 7. Raman spectrum of GaN; present are only the allowed Raman modes.

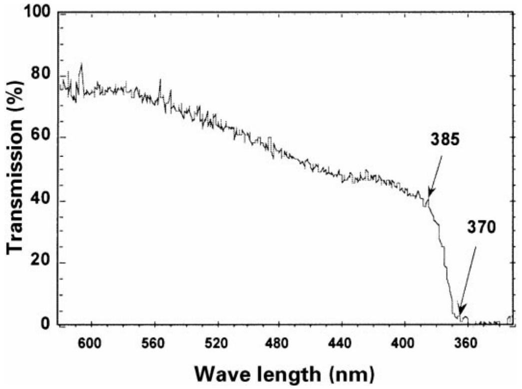

Fig. 8. Optical absorption spectrum of GaN. The absorption edge is at 369 nm and is about 10 nm wide.

A Raman spectrum acquired in a back scattering geometry from one of the grown GaN crystals is presented in Fig. 7. The spectrum exhibits only the allowed modes; this implies that the material lacks significant concentrations of structural defects or internal stress, which are known to relax the selection rules. The conservation of the selection rules is indicative of excellent crystallinity. The inset in this figure shows that the $E_2^{(2)}$ mode is at 567 cm^{-1} and has an FWHM of 3.5 cm^{-1}. These values are indicative of a material of the highest quality reported to date [22].

The results of the optical absorption study performed on a 300 μm thick crystal at room temperature are shown in Fig. 8. The absorption edge was positioned at 369 nm and was about 10 nm wide. The absorption coefficient over the wavelength range from 400 to 650 nm was estimated to be 50 cm^{-1}. A low absorption coefficient and a narrow absorption edge imply that the bulk GaN crystals are also of high optical quality. The slope in the visible part of the spectrum probably arose due to scattering on the unpolished crystal surface.

4. Summary

Growth of up to 3 mm long bulk GaN crystals was achieved via sublimation of cold pressed GaN pellets or evaporation of Ga metal in flowing NH_3. The experiments were conducted at a growth temperature, pressure, and NH_3 flow rate of 1000°C, 600 Torr and 50 sccm, respectively. The concentrations of all impurities but oxygen were below the detection limits of SIMS ($\leqslant 10^{16}$ atoms/cm^3); the concentration of oxygen was measured to be 3×10^{18} atoms/cm^3. Sharp bound exciton emission was observed in the PL spectra of these crystals; no yellow luminescence was observed. An optical absorption edge of 369 nm and an absorption coefficient in the visible spectrum of 50 cm^{-1} were determined. The Raman spectrum was in a complete agreement with the selection rules for the wurtzite structure and showed narrow and well-positioned peaks with the $E_2^{(2)}$ mode at 567 cm^{-1}. All these results confirm the excellent quality of the grown crystals.

Acknowledgements

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