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Submitted to the **Material Research Society Proceedings**
Session "Wide-Bandgap Electronic Devices"

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Prepared by the

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Managed by
UT-BATTELLE, LLC, for the
U.S. DEPARTMENT OF ENERGY
Under Contract DE-AC05-00OR22725

November 2001

Mat. Res. Soc. Symp. Vol. 622 © 2000 Materials Research Society

Single Crystal Growth of Gallium Nitride Substrates Using an High Pressure High Temperature Process

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ABSTRACT

The use of standard bulk semiconductor crystal growth processes for the production of GaN is prohibited by both the high melt temperature of GaN and thermal decomposition of the compound into Ga metal and N_2 gas. We have employed a novel hydrostatic pressure system to grow GaN crystals. A high temperature, ultra-high pressure process was developed using a solid-phase nitrogen source to form GaN crystals in a Ga metal melt. Using a thermal gradient diffusion process, in which nitrogen dissolves in the high temperature region of the metal melt and diffuses to the lower temperature, lower solubility region, high quality crystals up to ~1 mm in size were formed, as determined by SEM, X-ray diffraction and micro-Raman analysis.

INTRODUCTION

GaN has emerged as an important engineering material, and has generated a great deal of industrial interest because of its optical properties related to its wide, direct bandgap. Consistent growth of high quality, large area GaN substrates is a critical issue for the development of next-generation GaN-based optoelectronic and microwave devices. However, bulk GaN single-crystals can not be produced by standard methods used for most other semiconductors, such as Czochralski or Bridgman growth using stoichiometric melts. This is due its extremely high melting temperature (2800 K) and the very high equilibrium nitrogen pressure (45 kbar) associated with GaN at its melting temperature [1]. Growth of semiconductor quality crystals at these conditions is practically impossible. Therefore, GaN crystals must be grown by other methods that utilize lower temperatures.

Presently, three techniques may be regarded as the most promising to produce GaN bulk crystals and substrates: high gas pressure crystal growth using nitrogen over high temperature Ga metal [2-7], chloride-hydride vapor phase epitaxy (especially in combination with lateral regrowth) [8-11], and the sublimation sandwich technique [12]. The differences in the lattice parameters and the thermal expansion coefficients between the GaN film and the heteroepitaxial substrates used in the vapor-based methods result in relatively large defect densities. Dislocation densities for the state of the art GaN crystals grown by vapor phase techniques are in the range of 10^8 - 10^{10} cm^{-2}, which is approximately 4 to 6 orders of magnitude higher than that obtained in other optoelectronic materials such as GaAs, InP, etc. The high pressure gas process has produced large, free-standing crystals (approximately 0.6 x 15 x 15 mm) with relatively low dislocation densities (as low as 10^1 - 10^2 cm^{-2} [7]), but carries with it a need for highly specialized equipment for handling the dangerous, high gas pressure environment required for

crystal growth.

In this paper, we present a novel process for the synthesis of GaN crystals using high mechanical pressures and high temperatures. A solid pellet of pressed GaN was used as a nitrogen source, while new GaN crystals were formed in a Ga melt. This process differs significantly from other published work in that the system contains no free volume for an ambient gas.

EXPERIMENTAL DETAILS

Crystals were synthesized in an ultra-high pressure (UHP) crystal growth system. The apparatus used in this work is based on a split-sphere hydraulic system, shown schematically in Figure 1. Hemispherical hydraulic membranes apply pressure to a set of eight large steel dies, which in turn press upon a smaller set of six cemented tungsten carbide dies, finally applying an amplified pressure (resulting from the successive decrease in contact surface area) on a cubic reaction cell located at the center of the spherical region. Also included in Figure 1 is a schematic representation of the nature of the applied compressive stress on the reaction cell. The tri-axial compressive stress applied to the cell produces the hydrostatic pressure under which crystal growth proceeds in the Ga melt.

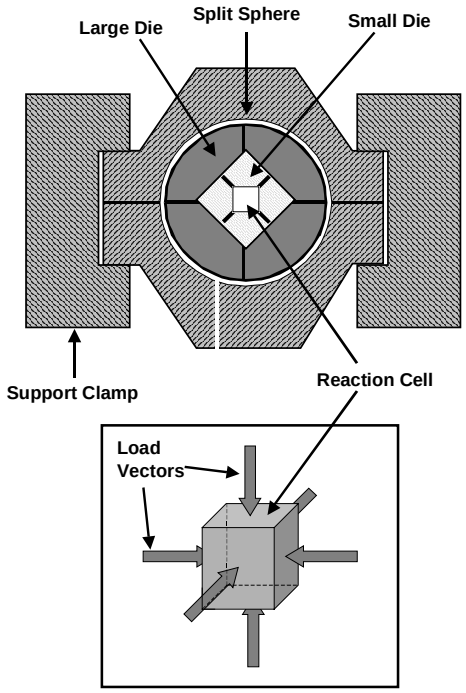

Figure 1. *Schematic diagram of UHP split sphere reactor illustrating applied mechanical loading of reactor core*

This system is capable of applying up to 65 kbar mechanical compression to a reaction cell while simultaneously heating the cell to greater than 1500 ºC. For this work, the cell contained pressed GaN powder, which acted as a source of nitrogen upon heating, and pure (99.99%) Ga metal as reactants. Crystal growth proceeded by first applying compressive mechanical loading of the reactor core to the desired pressure level, after which the cell temperature was ramped up to the desired value. Time-dependent heater power profiles were preprogrammed and controlled by computer. After processing, the reaction cell was extracted from the reactor, opened, and the remaining Ga metal dissolved in a HNO_3/HCl acid solution, leaving the GaN crystals available for collection and analysis. Crystal morphology was evaluated using SEM, while structural characteristics were evaluated using X-ray diffraction (XRD) and micro-Raman spectroscopy.

DISCUSSION

Multiple GaN crystals were formed during the course of each experiment as a result of spontaneous nucleation in the Ga metal melt under the conditions used. SEM micrographs of crystals synthesized in this UHP process are shown in Figure 2. These crystals exhibit plate-like morphologies suggestive of a hexagonal structure and are ~600 - 800 µm in size. Small (~10 µm) triangular growth features visible on the faces of the crystals displayed preferential orientation with respect to each other, suggesting either single crystal or highly textured growth. Dendritic and needle-like crystals were also commonly observed after processing. Energy dispersive X-ray spectroscopy (EDS) semi-quantitative analysis indicated that crystals formed in this process tended to be nitrogen deficient (N/Ga<1).

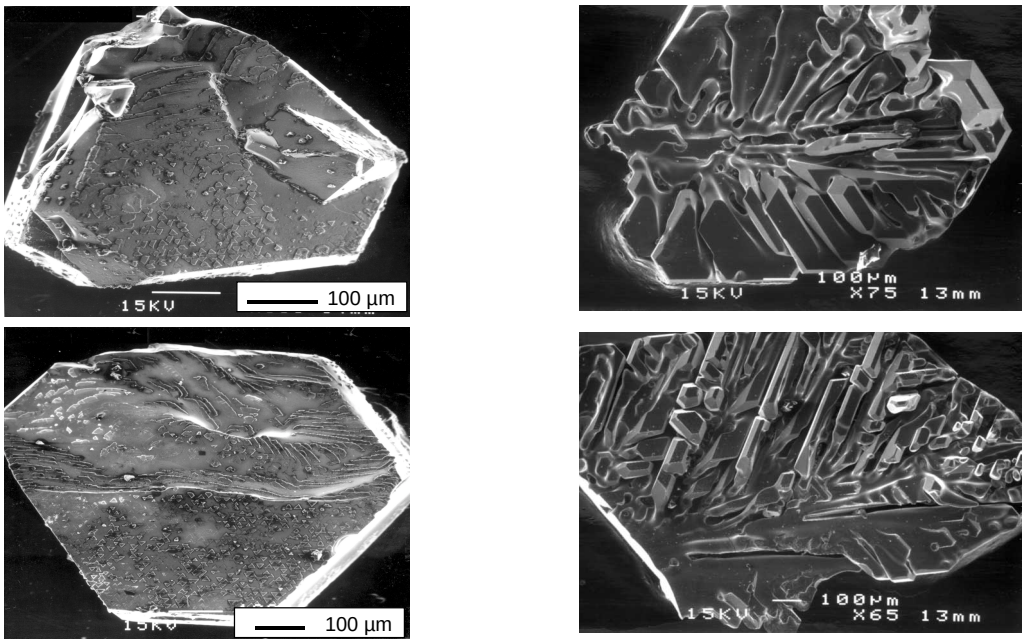

Figure 2. *SEM micrographs showing typical GaN crystals formed in UHP thermal gradient process.*

Structural characterization of the crystals was accomplished using XRD and micro-Raman spectroscopy. XRD was performed using a Rigaku Cu rotating anode target, a singly-bent (vertical focusing) LiF monochromator, and a four-circle Huber diffractometer (standard 2θ, θ, χ, and φ circles). Analysis showed the sample to be single-crystal hexagonal GaN with the broad face oriented parallel to (0001). The measured lattice parameters were: a=3.19 Å and c=5.186 Å, which are in good agreement with published values for GaN. A θ-scan rocking curve taken about the (0004) plane from this crystal is shown in Figure 3. The quality of the crystal was such that the rocking curve full-width-at-half-maximum (FWHM) was no wider than the resolution limit (108 arc sec) of the spectrometer, indicating a low defect density crystal. Acquisition of a φ-scan showed the (1 0 -1 0) planes spaced at regular 60° increments, further verifying the hexagonal structure.

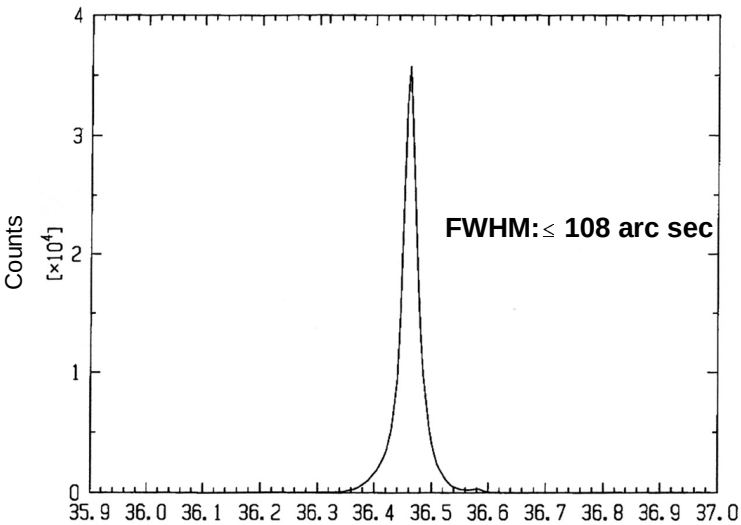

Figure 3. *XRD rocking curve taken about the (0004) plane from UHP grown GaN crystal.FWHM of the peak was resolution limited to 108 arc sec.*

A micro-Raman spectrum taken from the same crystal is shown in Figure 4. The Raman spectrum was taken in a backscattering mode using the 514 nm line of an Ar-ion laser at a spectral resolution of ~1 cm^{-1}. This spectrum shows the characteristic A_1(TO), A_1(LO), and E_2 modes of the hexagonal GaN structure at 528, 730 and 565 cm^{-1}, respectively. Asymmetry in the E_2 phonon mode peak was the result of a small, unresolved E_1(TO) mode peak at ~554 cm^{-1}. The A_1(LO) and E_2 modes are the theoretically allowed modes in the backscattering geometry. Presence of the weak A_1(TO) mode in the spectrum may be indicative of an imperfect backscattering alignment during spectral acquisition.

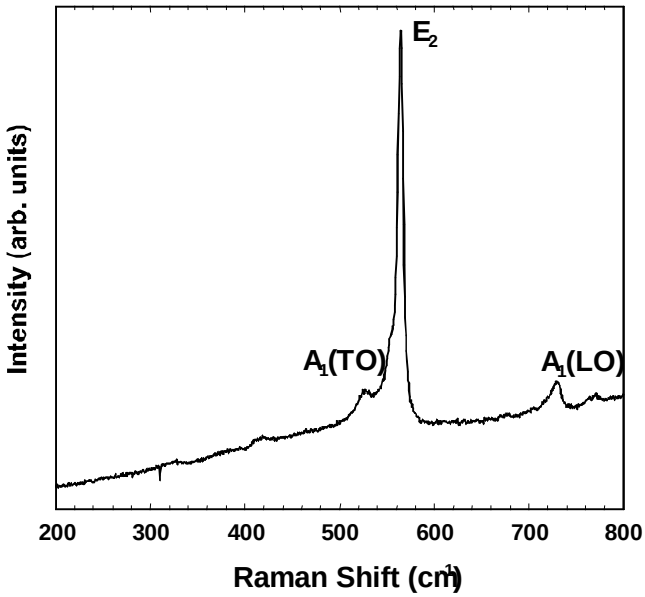

Figure 4. *Micro-Raman spectrum of UHP grown crystal showing characteristic GaN spectral features.*

CONCLUSIONS

The observed crystal growth in this work proceeded from spontaneously formed nuclei in the Ga melt. Atomic nitrogen was provided in the melt through the thermal dissolution/decomposition of the GaN source pellet at the operating pressure of the system, via the following process:

$$GaN_{(s)} \leftrightarrow Ga_{(melt)} + N_{(melt)}, \tag{1}$$

where $Ga_{(melt)}$ and $N_{(melt)}$ indicate gallium and nitrogen dissolved in the melt region. The reaction cell was designed to maintain a temperature gradient across the Ga melt region adjacent to the source pellet, keeping the GaN source in the highest temperature zone, thus allowing the dissolved nitrogen to diffuse to the lower temperature (lower solubility) region of the melt where it then reacted to form new GaN. The crystal growth rate is controlled by the flux of the dissolved nitrogen in the Ga melt in accordance with the expression:

$$J_N \propto \frac{\partial(c_N(x,T))}{\partial x}, \tag{2}$$

where J_N is the flux of dissolved nitrogen, and the right-hand term is the temperature dependent concentration gradient of the dissolved nitrogen. Nitrogen readily exceeded the supersaturation concentration necessary for spontaneous, homogeneous nucleation in these experiments. This is due to the very low solubility of nitrogen in Ga metal, which is only ~0.1% at a temperature of 1600 K and 32 kbar pressure [1]. Increasing the pressure and the temperature of the Ga melt results in increased nitrogen solubility for faster growth due to the increased flux. Under the experimental conditions used, we expect the otherwise thermodynamically favored reaction:

$$N_{(melt)} + N_{(melt)} \leftrightarrow N_{2\,(g)} \tag{3}$$

to be suppressed inside the reaction zone because of the large activation barrier associated with the high applied mechanical pressure and lack of free volume. By carefully controlling the nitrogen solubility via the temperature gradient in the melt, as well as providing a pre-existing seed crystal in the lowest temperature region to suppress homogeneous nucleation, we expect that much larger, high quality crystals may be grown using this process.

ACKNOWLEDGEMENTS

We would like to acknowledge the valuable assistance of S. MacDonald of the University of Florida for the acquisition of micro-Raman spectral data. Working in collaboration with the University of Florida, The Gemesis Corporation conducted its work under SBIR Grant No. N00014-99-M-0151, which was monitored by Colin Wood of the Office of Naval Research.

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