Quarterly Letter Report

Growth of Single Crystals and Fabrication of GaN and AlN Wafers

Supported under Grant # N00014-00-1-0192
Office of the Chief of Naval Research
Report for the period 7/1/00-9/30/00

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DTIC QUALITY INSPECTED 4

20001025 060

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
July, 2000

3. REPORT TYPE AND DATES COVERED
Semiannual: 1/1/00 - 6/30/00

4. TITLE AND SUBTITLE
Growth of Single Crystals and Fabrication of GaN and AlN Wafers

5. FUNDING NUMBERS
CFDA: 12.300
DUNS: 008963233
PR: 00PR03598-00
Act.:00312--0051
CAGE: 0ECY3
EDI: 7129AB

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8. PERFORMING ORGANIZATION REPORT NUMBER
N00014-00-1-0192

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)
Sponsoring: ONR, Code 312, 800 N. Quincy, Arlington, VA 22217-5660
Monitoring: Administrative Contracting Officer, Regional Office Atlanta
Atlanta Regional Office
100 Alabama Street, Suite 4R15
Atlanta, GA 30303

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
GaN and AlN single crystals were grown from the vapor phase by evaporation of gallium or aluminum metals under an ammonia or nitrogen flow in a high temperature reactor. A growth rate of 500 μm/hr in the c direction was achieved for GaN while the growth rates for AlN were as high as a few millimeters per hour. The crystal size reached 3 mm for GaN and up to 15 mm for AlN. For both materials, the crystal aspect ratio (c/a) could be controlled by temperature and partial pressure of reactants. The resulting crystals were transparent and of excellent crystalline quality, as confirmed by x-ray diffraction, Raman scattering, and transmission electron microscopy studies. Photoluminescence studies on GaN conducted at 77 K showed a sharp emission peak centered at 359 nm. Time dependent photoluminescence measurements revealed optical metastability in bulk GaN.

14. SUBJECT TERMS
GaN, AlN, bulk crystal growth, growth from vapor phase, photoluminescence, optical absorption, Raman, SIMS.

15. NUMBER OF PAGES
30

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLAS	UNCLAS	UNCLAS	SAR

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Growth of AlN bulk crystals from the vapor phase

Introduction

The following report summarizes research activities of the past quarter (07-09 2000). As stated in earlier reports, the goal of this project is the growth of high-quality AlN bulk crystals from the vapor phase. The equipment used for this purpose has been described previously. Apart from routine maintenance, no major hardware changes were required in the past quarter. After successfully testing the growth equipment, and after completing a series of initial, unseeded growth runs our research efforts focussed on (1) a systematic study of the relevant growth parameters and (2) first seeded growth experiments.

Experimental details

Al source material: A first series of experiments had shown that AlN crystals grew at large growth rates from pure Al source material. However, it was found that Al-rich AlN crust typically formed within the first hour of growth at the Al source surface and considerably reduced the Al vapor pressure, thus slowing down the AlN growth rates. In the preparation of long-term growth experiments (24 hours or longer) mentioned, AlN crust formation issue had to be addressed. Under the current experimental conditions, it appears to be difficult, if not impossible, to avoid the formation of the AlN crust. In order to obtain a constant Al evaporation rate, we decided to use pre-reacted AlN as a source material. For this purpose, larger amounts of Al (typically 10 g) were heated for 2 hours to 2000°C in a 500 Torr nitrogen atmosphere, in order to purposefully form a thick AlN crust over the source material. Subsequently, the same source material was used for high-temperature AlN growth runs. Although the Al vapor pressure from AlN sources is considerably smaller than that of pure Al, constant growth rates could be achieved over extended periods of time. The lower growth rates were partially compensated by increasing the source temperature to 2300°C.

Seeded growth experiments: AlN crystals formed during initial growth runs were used as seeds. Seeds were installed in the top part of the growth crucible by mechanically wedging the seeds into the relatively soft BN cap material. Typically, needle-shaped seeds of several mm in length and an aspect ratio of ~10:1 were used for these experiments. Optical micrographs of the seeds were taken before and after the growth. The seeds were installed as grown; surfaces were neither polished nor chemically treated.

Experimental results

Growth parameter optimization: The following growth parameters were optimized for the use of AlN source materials: growth temperature (i.e., the temperature of the graphite heater as measured using an optical pyrometer), system pressure, crucible position (and resulting changes in the temperature gradient between source material and AlN seeds). Nitrogen flow rates were found to be of minor influence and were subsequently kept constant at 100 sccm. Mass loss of the source material occurred from 1800°C on, and reached 150 mg/hr at 2300°C. System pressure was found to influence the distribution of crystal growth inside the growth crucible. Growth at lower pressure (100 Torr) yielded enhanced growth in the crucible cap (due to a longer mean free path of the Al species); however, in order to avoid long-term decomposition of the BN reaction tube and crucible, most growth runs were performed at a higher nitrogen pressure (500 Torr).

Long-term growth runs of 24 hours were performed under the following conditions:

Heater temperature	T = 2300°C
System pressure	p = 500 Torr
Temperature gradient	~ 50°C/inch

Spontaneous nucleation: Fig. 1 shows a picture of a crystal grown under the above growth conditions. In each growth experiment several crystals of similar size and surface morphology grew by spontaneous nucleation off the BN crucible walls, at a distance of

about one inch from the AlN source. Several growth runs using identical parameters confirmed reproducibility of the growth conditions.

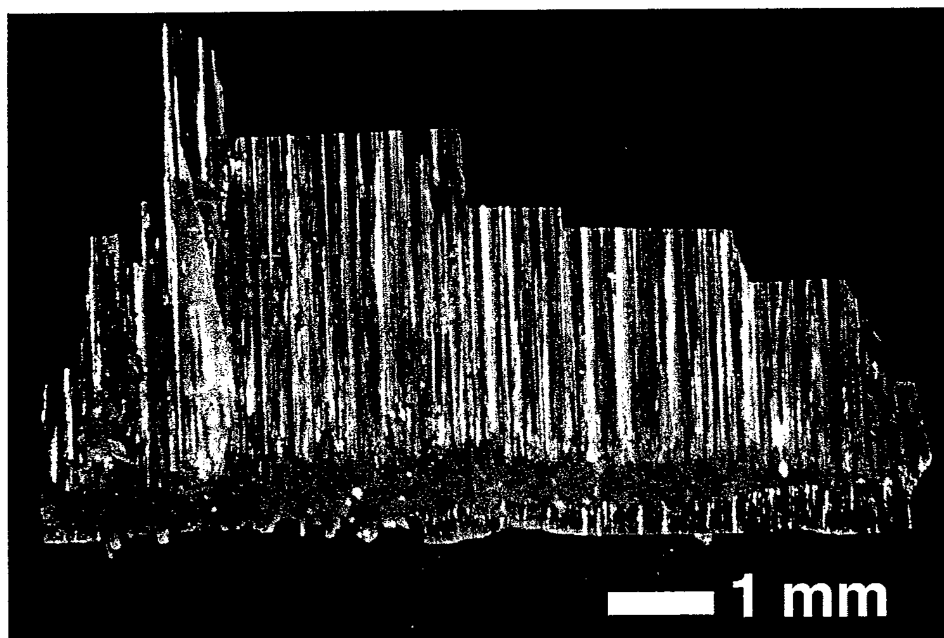


Fig.1: AlN crystal grown from AlN source at T = 2300°C, p = 500 Torr. Crystal size: 8 x 4 x 0.7 mm^3.

Under the given growth conditions, spontaneously nucleated crystals up to 20 mm in length were grown in 24 hours. Most crystals showed a striated surface morphology. The crystallographic c-axis was found to be oriented parallel to the surface striations. The crystals were optically transparent. In some cases, a slight blue coloration appeared close to the nucleation site of the crystal, indicating that at the beginning of the growth a larger concentration of contaminants might have been present.

<u>Seeded growth:</u> Using spontaneously nucleated crystals from earlier growth runs, we demonstrated continued growth on AlN seeds. Fig. 2 shows a sequence of pictures illustrating seeded AlN growth under the aforementioned growth conditions. As can be seen, the seed kept growing even after having been removed from the system and exposed to air several times.

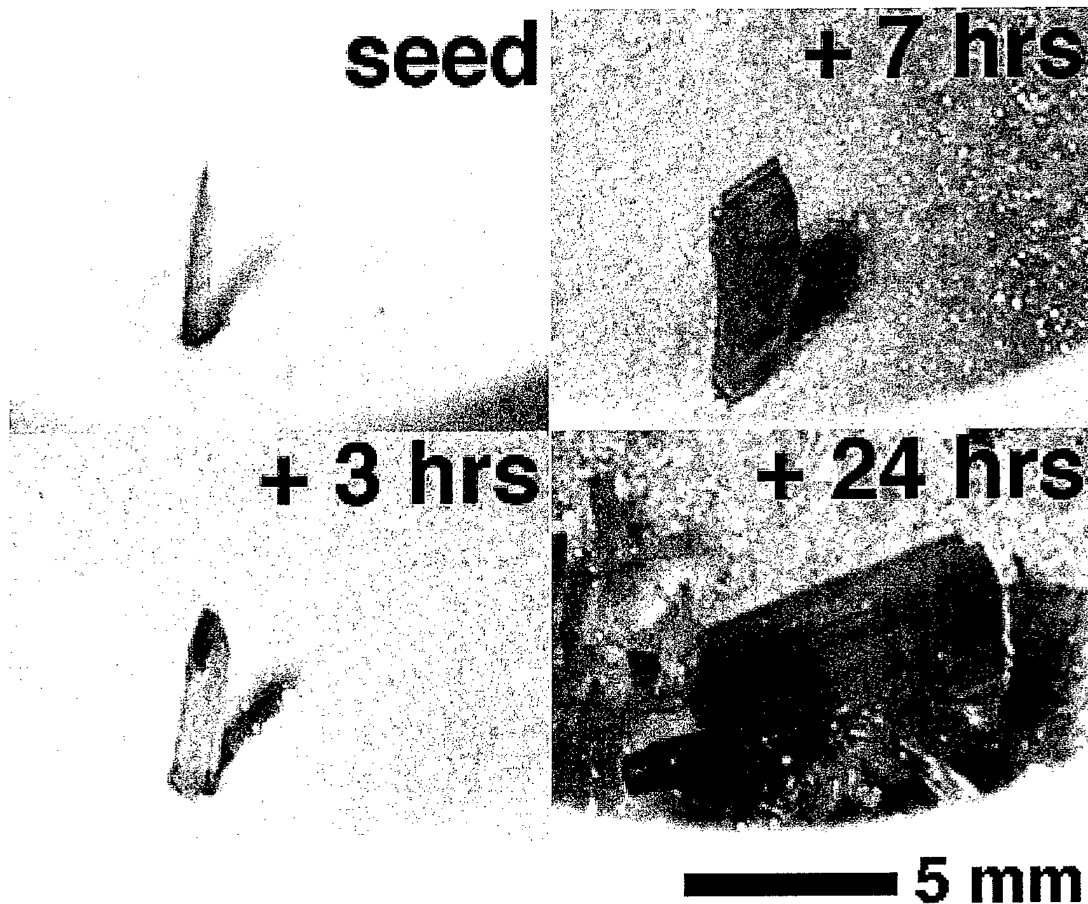


Fig.2 Seeded AlN growth. From top to bottom: AlN seed as installed in growth crucible, growth of AlN crystal at 2300°C after 3 hours, after 7 additional hours, and after 24 additional hours. Seed size: 5 x 0.4 x 0.5 mm^3. Final crystal size: 6 x 1 x 6 mm^3

The volume of the AlN crystal increased more than 30 fold in 34 hours of growth time. Apart from some secondary nucleation that occurred during the last growth step, the bulk of the obtained crystal was single crystalline. This finding indicates that interrupting the growth (e.g., to refill the source material) is feasible, a fact that may be of crucial importance for the fabrication of larger crystals.

Conclusion

In the past quarter, we have focussed on the growth from AlN source material. We have achieved stable and reproducible, long-term growth conditions. First experiments on seeded

growth have been successfully accomplished and have shown that the growth process can be continued after the growth surfaces had been exposed to air, and that crystals keep growing as a function of time.

Growth of GaN bulk crystals from the vapor phase

Introduction

In this research effort, a high temperature nucleation technique has been developed to grow GaN crystals. Processing conditions for lateral and vertical growth have been determined, and have been applied to seeded growth experiments. Seeded growth was accomplished by using seed crystals grown by the mentioned high temperature nucleation technique, in an effort to produce larger GaN crystals without secondary nucleation.

Experimental details

Growth experiments were conducted in a dedicated dual-heater vertical furnace. The growth crucible was made out of hot-pressed BN. The metallic Ga source material was loaded in a separate BN insert. The temperature of the BN substrate, located at the center of the crucible, was lowered using a water-cooled stage in order to achieve a favorable temperature gradient. Spurious nucleation of GaN, which typically occurs during the temperature ramp-up, could be avoided by heating the growth system to 1260°C in an N_2 ambient, in order to avoid reaction of Ga and NH_3. The growth process was initiated thereafter by flowing NH_3 and decreasing the substrate temperature.

Experimental results

Preliminary experiments showed that the optimum growth temperature in the current growth system is 1130°C. To determine the optimum processing parameters for the vertical growth and the lateral growth at 1130°C, crystal aspect ratios were experimentally determined as a function of the total pressure and the NH_3 flow rate during the growth, see Fig. 1. Crystals with high aspect ratios were obtained at higher total pressures (> 500 Torr). The influence of the NH_3 flow rate on the aspect ratio is pronounced at higher pressures, but less significant at lower pressures.

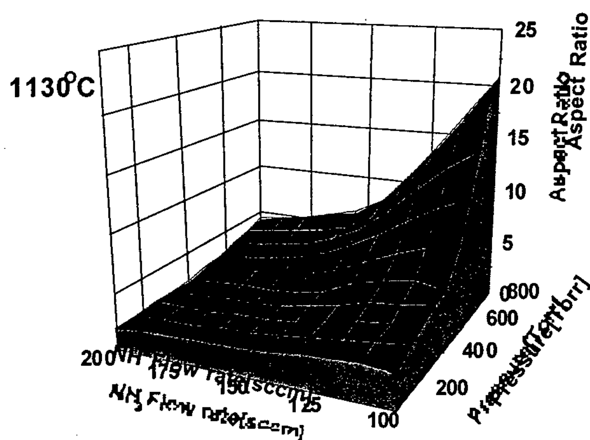
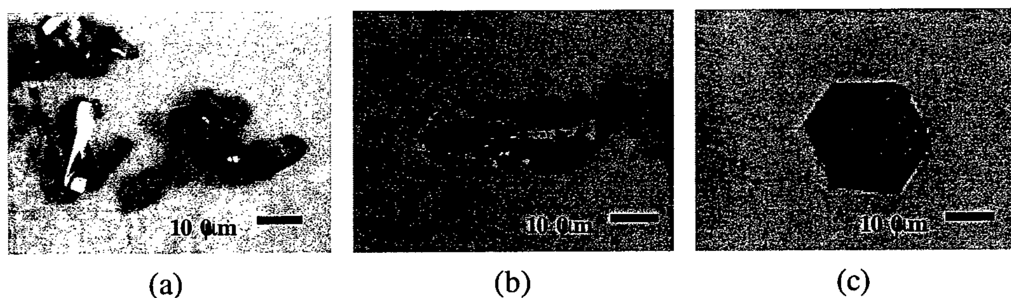


Fig. 1: GaN crystal aspect ratio as a function of ammonia flow rate and system pressure. Growth temperature: 1130°C.

Further investigations showed that the aspect ratio change could be related to the depletion of Ga concentration in the vapor phase due to the higher velocity of the NH_3 stream at larger flow rates. Therefore, it is more accurate to interpret the aspect ratio changes in terms of the NH_3/Ga ratio rather than the total pressure. At lower pressures of NH_3, the ammonia density decreases and the Ga flux increases due to the increased mean free path in the vapor phase.

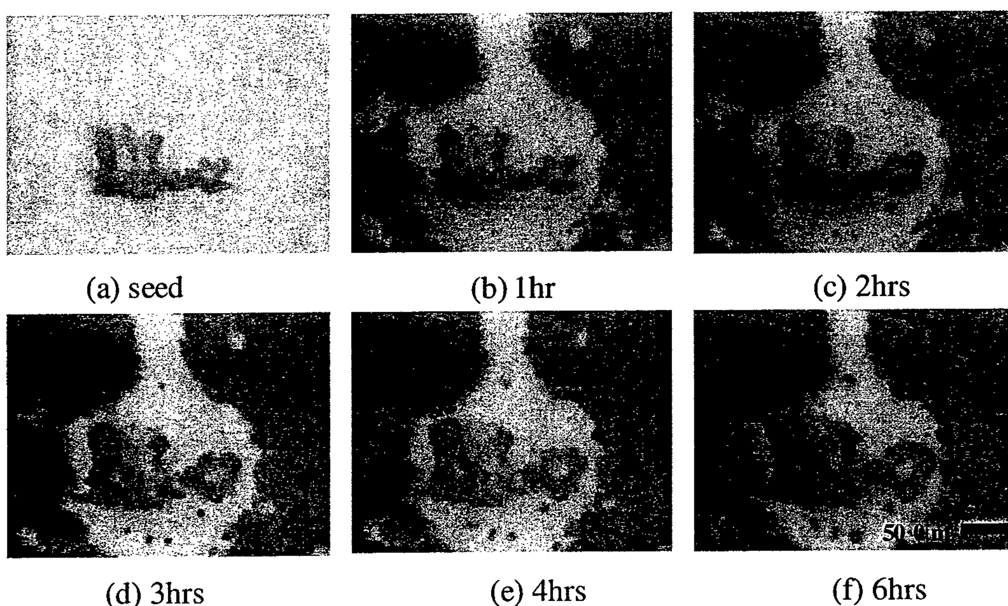
In order to grow GaN platelets, low NH_3/Ga ratios were needed. To obtain a larger Ga flux to the substrate, the NH_3 gas inlet was moved from 1" to 2" away from the substrate surface. Figure 2 shows the change in crystal morphology as a function of the Ga source temperature. GaN platelets were obtained at a source temperature of 1260°C, a total pressure of 430 Torr, and a flow rate of 50 sccm of NH_3. As the total pressure was increased, the crystal morphology changed from platelets to needles. Prolonged growth resulted in larger crystal sizes, but multiple spontaneous nucleation was still a problem.



(a) (b) (c)

Fig.2: Crystal morphology change with the Ga source temperature, (a) 1240°C, (b) 1250°C, and (c) 1260°C

To grow larger GaN crystals without secondary nucleation, seeded growth was conducted. GaN crystals of both large and small aspect ratios were used as seeds. Figure 3 shows results of optical in-situ monitoring of a growth experiment, in which GaN needles were used as seeds. Growth parameters were optimized for lateral growth conditions. As can be seen in the micrographs, a nucleation exclusion zone was formed around the seed crystals. The seed crystals grew without secondary nucleation for six hours. The width of the crystals increased with time while the length of the crystals remained nearly unchanged.



(a) seed (b) 1hr (c) 2hrs

(d) 3hrs (e) 4hrs (f) 6hrs

Fig. 3: In-situ monitoring of the seeded growth of GaN needles at 1130°C, 430 Torr and 60 sccm of NH_3.

Fig. 4 compares the morphology of the crystals grown from seeds with spontaneously nucleated crystals that formed on the BN substrate during the same growth run. The latter crystals were all platelets, as shown in Fig. 4(b) and (c). Both the seed crystals and the spontaneously nucleated crystals showed a smooth surface morphology, see Fig. 4 (c), (d), and (e). Raman spectrum for a 400μm wide and 500μm long crystal grown from a seed crystal confirmed excellent crystallinity.

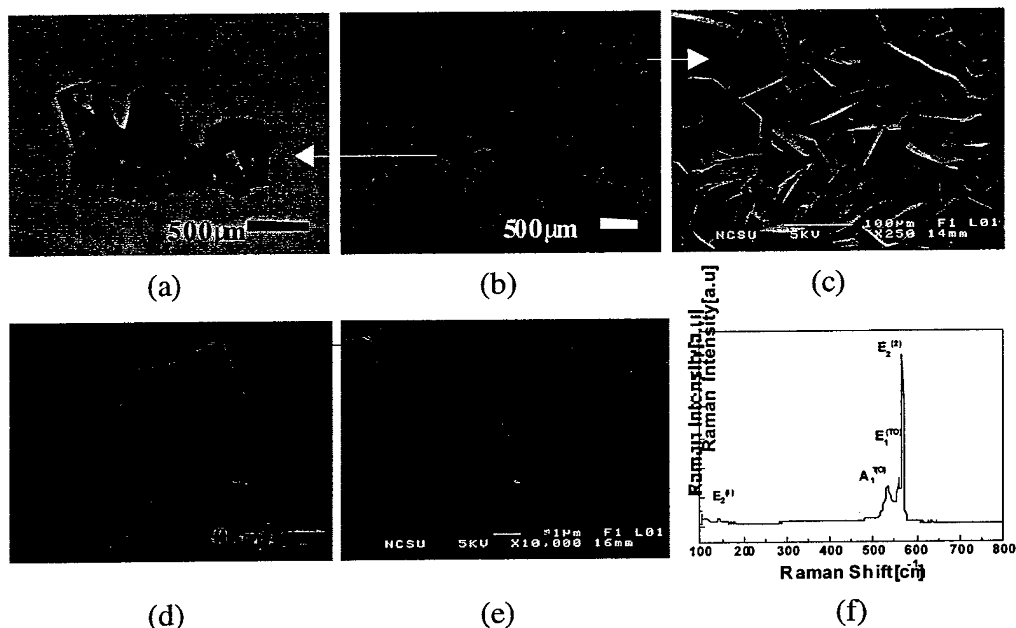


Fig. 4: Seeded growth of GaN needles at 1130°C, 430 Torr and 60 sccm of NH_3. (a) Optical micrograph of a GaN crystal cluster after the seeded growth, (b) Crystals on BN after growth, (c) SEM micrograph of the crystals grown on BN, (d) Magnified view of a crystal in (a), (e) SEM micrograph of the surface, (f) Raman spectrum of the crystal in (d).

Conclusion

Systematic studies have revealed the optimum growth parameters for the growth of both high aspect ratio GaN crystals (needles) and low aspect ratio crystals (c-plates). We have successfully demonstrated seeded growth of GaN crystals. We are currently investigating the effect of the supersaturation of the vapor phase to isolate the growth predominantly on the seed crystal. We have recently grown 2mm long and 1.5mm wide GaN crystals via

seeded growth. In addition, we are planning to investigate GaN growth using diluted ammonia in nitrogen.

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