

Journal of Crystal Growth 179 (1997) 363-370

JOURNAL OF CRYSTAL GROWTH

# Sublimation growth and characterization of bulk aluminum nitride single crystals

# Cengiz M. Balkaş<sup>a</sup>, Zlatko Sitar<sup>a</sup>, Tsvetanka Zheleva<sup>a</sup>, L. Bergman<sup>b</sup>, R. Nemanich<sup>b</sup>, R.F. Davis<sup>a.\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7907, USA <sup>b</sup> Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-7907, USA

Received 18 February 1997

#### Abstract

Single crystalline platelets of aluminum nitride (AlN)  $\leq 1$  mm thick have been grown within the temperature range of 1950–2250°C on  $10 \times 10$  mm<sup>2</sup>  $\alpha$ (6H)-silicon carbide (SiC) substrates via sublimation-recondensation in a resistively heated graphite furnace. The source material was sintered AlN. A maximum growth rate of 500 µm/h was achieved at 2150°C and a source-to-seed separation of 4 mm. Growth rates below 2000°C were approximately one order of magnitude lower. Crystals grown at high temperatures ranged in color from blue to green due to the incorporation of Si and C from the SiC substrates; those grown at lower temperatures were colorless and transparent. Secondary-ion mass spectroscopy (SIMS) results showed almost a two order of magnitude decrease in the concentrations of these two impurities in the transparent crystals. Plan view transmission electron microscopy (TEM) of these crystals showed no line or planar defects. Raman spectroscopy and X-ray diffraction (XRD) studies indicated a strain free material.

#### 1. Introduction

Aluminum nitride is a wide band gap semiconductor with an energy gap of 6.2 eV. It has a high thermal conductivity (2 W/cm K) [1] and possesses the highest ever reported surface acoustic wave (SAW) velocity [2]. At present time, it is being used in thin film form as a buffer layer on which other III-V nitrides are deposited and in polycrystalline bulk form as a candidate insulator material for integrated circuit packages. It is also a candidate for selected piezoelectric applications and SAW devices. However, its potential in some of these and other applications has been hampered by the lack of bulk single crystals, as discussed in several review articles [3–6].

Growth of AlN crystals by sublimation/recondensation [7–13], evaporation/reaction [14] and solution routes [15, 16] has been investigated in several laboratories. Slack and McNelly [7, 8] achieved crystals up to 1 cm long by 0.3 cm diameter via sublimation/recondensation. The source material was prepared via reaction between Al

<sup>\*</sup>Corresponding author. Fax: +1 919 515 7724; e-mail: davis@mat.mte.ncsu.edu.

and  $N_2$  at 1850°C. The subsequently grown crystals were hexagonal, amber in color and grew predominantly along the *c*-axis at a growth rate of 300 µm/h at 2250°C. Reaction of the Al vapor with crucible materials seriously hampered the growth of larger crystals. Pastrñák and Roskovcová [14] achieved crystals 3-5 mm in length and less than 1 mm in diameter using the evaporation/reaction technique. Solution growth has been limited by the availability of a solvent that could both dissolve AlN at appreciable rates and remain inert to reaction with the container. An experimental study of this method for growing AlN single crystals by spontaneous nucleation has been conducted by Dugger [15, 16] using a AlN-Ca<sub>3</sub>N<sub>2</sub> solution contained in graphite crucibles. The solution was cooled from  $1550^{\circ}C$  at  $2^{\circ}/h$  for 26 h. Small (1.1 mm long  $\times$  0.3 mm diameter) AlN crystals were obtained via nucleation on the crucible walls.

To date, no attempt has been made to grow bulk AlN crystals on a substrate. We report herein for the first time the seeded growth of AlN using 6H–SiC substrates. The following sections provide the experimental detail and discuss the results of the various analyses of the grown material.

# 2. Experimental technique

# 2.1. Sublimation of AlN

Most metal nitrides evaporate primarily by decomposition to their elements because of the high molecular stability of  $N_2$  which forms on and desorbs from the surface of the heated nitride. Theoretical and analytical investigations regarding the sublimation behavior of AlN [12, 17, 18] have shown that it evaporates according to the reaction:

$$2AIN(s) = 2AI(g) + N_2(g).$$
(1)

Although thermodynamical models based on free energy calculations indicate that a small amount of AlN (g) should exist upon sublimation [19], no experimental observation of gaseous AlN has been reported. Therefore, one can assume that the reaction governing the recondensation process will be the reverse of reaction (1). If  $N_2$  is continuously replenished during the sublimation experiments, then the availability of Al (g) at the growth surface will be the rate limiting factor for the growth of AlN. By establishing a temperature gradient between the source and the seed, a net Al (g) flux, originating from the hotter site, can be obtained. In this case, the growth rate will be proportional to the equilibrium partial pressure difference of the Al (g) above the source and the seed surfaces.

#### 2.2. Growth apparatus

Sublimation experiments were conducted in a resistively heated graphite furnace capable of 2250°C and temperature gradients required by the process. A sketch of the experimental configuration of the crucible and growth assembly are shown in Fig. 1. An important feature of the growth system was the capability of changing the axial position of the seed crystal with respect to the source and heater.



Fig. 1. Schematic of the graphite growth assembly employed in the sublimation growth of AlN.

# 2.3. Crucible selection

A crucial technical issue in the sublimation of AlN was the selection of the crucible material. Physical and chemical stability at very high temperatures, machinability, and compatibility with the furnace components and atmosphere, as well as the source and seed, were considered. The difficulty of finding a material that would satisfy these criteria was discussed extensively by Slack and McNelly [1]. Initial experiments with graphite resulted in severe degradation of the crucible components. Aluminum carbide  $(Al_4C_3)$  was formed even at temperatures below 1900°C. Above 1900°C, large pits and loose carbon powder were found within the crucibles possibly as a result of the formation and subsequent decomposition of  $Al_{4}C_{3}$ .

Since the incompatibility with Al vapor was the only disadvantage of the graphite crucibles, they were coated with SiC via chemical vapor deposition. Although the crucible stability improved, the SiC coating also had a finite lifetime. Aluminum vapor slowly diffused through the SiC barrier, reacted with the graphite at the interface and eventually caused the coating to spall. However, the lifetime of the coating was sufficient to conduct several 10–15 h experiments.

#### 2.4. Source material and seed crystals

Bulk AlN (99% dense) blocks produced via sintering without additives were used as the source material. The desired ceramic was chosen over loose powder to reduce contamination from the surface oxide and hydroxides, to achieve a more stable sublimation rate, and to allow precise separation between the source and the seed. The sourceto-seed distance was crucial for the achievement of crystal growth. The source was positioned in the isothermal section of the furnace to ensure an essentially constant evaporation rate.

The choice of the seed crystals was very limited due to the high temperatures needed to achieve surface diffusion rates sufficient for rapid crystal growth. Single crystal, 6H-SiC (0001) wafers (10 mm × 10 mm) were used as seeds in all experiments, due to the relatively small lattice mismatch to AlN (0.9%) and high temperature stability. The seed crystals were heated in vacuum at  $\approx 1150^{\circ}$ C prior to crystal growth to desorb the surface oxide, hydrocarbons and any other contaminants.

# 2.5. Growth conditions

All experiments were performed under a 100 sccm flow of ultra-high purity N<sub>2</sub>. The background pressure was maintained at 500 torr by an automatic throttle valve. The temperature ranges of 2100-2250°C and 1950-2050°C were investigated consecutively. At these temperatures, the sublimation rate varied from approximately 10 to 200 mg/h. The lower temperature range was employed primarily because of the degradation of the furnace and the seed crystals at the higher temperatures. In both cases, a temperature difference of 80-150°C was obtained between the source and the seed, depending on the separation distance.

The separation distance between the source and seed ranged from 1 to 40 mm. The range from 1 to 5 mm was found to be optimal for all temperatures employed in this study. Distances  $\ge 5$  mm resulted in a considerable reduction in growth rates, primarily due to diffusion effects in the gas phase but also due to an increased probability of parasitic reactions. The growth rate at a separation of 3 mm was  $\approx 30$  times higher than at a 15 mm separation. Precise and repeatable separation distances were found to be important for the control of the thermal gradient and incident flux of evaporated material onto the substrate. The use of hot pressed AlN was found to be very beneficial for these adjustments. The AlN source was re-positioned to the desired source height before each experiment.

#### 2.6. Characterization

The as-grown AlN bulk crystals were first characterized via optical microscopy. Color, size, transparency, and macrostructural features were observed at magnifications of 5X-40X. The crystalline quality was determined by TEM and XRD. The former studies were performed using a TOPCON EM-002B, operating at 200 kV. *C*-axis oriented TEM samples were prepared by grinding and polishing the bulk AIN crystals to a thickness of 100  $\mu$ m, dimpling to a thickness of 20  $\mu$ m and Ar<sup>+</sup>-ion milling to electron transparency.

X-ray diffraction measurements were conducted using an X'pert model Philips Materials Research Diffractometer. Theta-2 theta scans were taken in a symmetric configuration using  $Cu-K_{\alpha}$  radiation and a graphite monochromator.

X-ray Photoelectron Spectroscopy (XPS) was used to determine the stoichiometry of the AlN source ceramics before and after the growth. For that purpose, VG Microtech CLAM II hemispherical electron spectrometer and a Mg anode X-ray source were used.

Micro-Raman spectra were obtained at RT using back scattering geometry and the 514.5 nm line of an Ar laser. The spot size and spectral resolution were 4  $\mu$ m and 2 1/cm, respectively.

The SIMS data were acquired using Cameca IMS-6f and 10 keV  $O_2^+$  primary ion beam rastered over a 100  $\mu$ m<sup>2</sup> area. The  $O_2^+$  current was varied from 10 to 100 nA to obtain optimum secondary ion signal levels. The samples were biased at 4500 V, and the concentrations of C, O, Al (matrix reference signal) and Si were determined. The mass spectrometer was tuned to a sufficient mass resolution (approximately 2200 m/ $\Delta$ m) to allow the detection of Si and the rejection of AlH and all other pertinent interference signals.

# 3. Results and discussion

#### 3.1. General comments

In all experiments, crystalline AlN deposits were observed on most parts surrounding the AlN source; however, the majority of the deposition occurred on the seed crystal and the seed holder. Deposits on the crucible walls and the seed holder consisted of many individual hexagonal bars and platelets of single crystalline AlN. Separation of the AlN crystals from the SiC seeds was commonly observed in the material cooled from all growth temperatures. Analysis of the source material via XPS showed no change in the near surface stoichiometry as a result of evaporation. This is in agreement with the X-ray diffraction studies by Dreger et al. [20] conducted on AlN powders during evaporation. The source material was observed to have a slight reduction in height.

# 3.2. Growth in the $2100-2250^{\circ}C$ range

Single crystals of AlN having a thickness to one millimeter and covering the whole seed were obtained at a source temperature of 2150°C and a 4 mm source-to-seed separation. An optical micrograph of a representative sample which had separated from the SiC seed is shown in Fig. 2. The growth rate was estimated to be 0.5 mm/h. The results of XRD and Laue back reflection studies confirmed the monocrystallinity. The SiC seeds became light gray during the experiments performed between 2100 and 2150°C due to the partial evaporation of Si.

At growth temperatures between  $2150-2250^{\circ}$ C several  $\approx 2 \times 2$  mm individual hexagonal crystals were obtained on the seeds, since at these temperatures, severe degradation of the SiC substrates resulted in isolated stable nucleation sites. These crystals ranged in color from green to blue. The coloration strongly indicated the incorporation of impurities which were confirmed via SIMS analysis to be carbon and silicon from the SiC substrates. Fig. 3 shows a comparison of Si, C and O impurity levels in selected blue, green and transparent AlN crystals. The transparent crystal had almost two orders of magnitude less Si and C than the green, and blue crystals:

Upon cooling, the AlN crystals frequently delaminated and cracked, as can be observed in Fig. 2. This was most probably due to the mismatch in the coefficients of thermal expansion between the two materials; however, intrinsic stress in the deposited material and/or the extension of preexisting cracks at the edges of the SiC substrates may also have contributed to these phenomenon. Unfortunately, the thermal expansion coefficients data for these materials are not available for the entire temperature range of the experiments. Since AlN boules will ultimately be grown on obtained AlN crystals, this cracking problem should not be a significant barrier to the attainment of much larger crystals. Similar to the individual crystals



Fig. 2. Optical micrograph of an AlN single crystal grown at 2150 C and a 4 mm source-to-seed separation. Ruler in the bottom right corner has 1 mm marks.

Fig. 4. Optical micrograph of a single crystal of AlN grown at 1950 C and a 4 mm source-to-seed separation. Ruler on the left has 1 mm marks.



Fig. 3. Comparison of Si, C and O levels in different color AIN crystals.

the color of the AlN platelets grown within this temperature interval varied from dark blue to dark green.

#### 3.3. Growth in the 1950–2050 C range

Growth of AlN in the temperature range of 1950 to 2050°C was investigated both to prevent seed deterioration and increase crucible lifetime. Complete structural and chemical stability of the SiC seeds and significant reduction in the deterioration of the SiC coated crucibles were attained. Crystals grown in this temperature range were always colorless regardless of the morphology or growth site. Typical growth rates were reduced to  $30-50 \,\mu\text{m/h}$ . Growth runs of 10-15 h yielded 0.3-0.5 mm thick crystals on 1 cm<sup>2</sup> SiC substrates. A 0.4 mm thick transparent AIN platelet grown at 1975 C can be seen in Fig. 4. Unfortunately cracking occurred in these crystals as well and presumably for the same reasons stated in the previous subsection. Crystals grown in both temperature ranges had very smooth surfaces (average RMS = 6 Å) as determined by atomic force microscopy.

All crystals showed strong and well defined single crystalline XRD patterns. Only the (0 0 2) reflection, positioned at 36°, was observed in symmetric  $\Theta$ -2 $\Theta$  scans, as shown in Fig. 5 for a crystal grown at 1950°C. This suggested that the residual stress level in these crystals was low.

A bright field, plan view TEM micrograph taken along the [0001] direction and associated selected area diffraction (SAD) pattern are shown in Fig. 6. Uniform contrast density was observed



Fig. 5. XRD of bulk AlN showing only the  $(0\ 0\ 2)$  reflection parallel to the surface of the crystal.



Fig. 6. TEM image and SAD pattern of an AlN single crystal. The beam direction was along [0001].

throughout the specimen, indicating excellent quality single-crystalline AlN. No low angle boundaries, stacking faults or twinned regions were observed. The SAD pattern supports these results in that the diffraction spots are without arcs, which would indicate misoriented grains or streaks which are indicative of twinning and stacking faults.

A Raman spectrum acquired in a back scattering geometry from the (0001) face of an transparent AlN bulk crystal grown at 1950°C is presented in Fig. 7. The spectrum exhibits the allowed modes for this geometry:  $A_1(\text{LO}) \approx 893 \text{ 1/cm}, E_2^{(1)} \approx$ 250 1/cm,  $E_2^{(2)} \approx 660$  1/cm [21]. Since no forbidden modes could be detected, the AlN crystal had a well defined (0001) face of the wurtzite structure and did not exhibit significant concentrations of structural defects or internal stress which might have relaxed the selection rules. The inset of Fig. 7 shows a high resolution spectrum of the  $E_2^{(2)}$  mode. The FWHM of the  $E_2^{(2)}$  peak was  $7.0 \pm 0.5$  cm<sup>-1</sup>; the spectrum taken from a blue crystal grown at 2200°C the same peak had a FWHM value of  $9.5 \pm 0.5$  1/cm. This difference complements the results obtained by the SIMS analysis in which the colored crystals contained two orders of magnitude more Si and C than the transparent crystals.



Fig. 7. Raman spectrum of transparent bulk AlN grown at 1950 C.

It was observed that the maximum growth time was determined by the difference between the evaporation and condensation rates of AlN. In the sublimation/recondensation process there are two fluxes that must be considered; (1) that from the polycrystalline source to the substrate and (2) that resulting from evaporation of the growing crystal. During the early stages of the process the first is greater than the second; thus, a net deposition on the seed is expected. However, not all Al and N atoms that leave the surface of the source are adsorbed on the growth surface to form AIN. Therefore with time the distance between the source and substrate increases and, as stated above, the growth efficiency dropped rapidly. Finally, the amount of evaporating AIN exceeded the amount of depositing material. Thus, experiments performed for extended periods of time resulted in a gradual reduction in growth rates or loss of previously grown material.

#### 4. Summary

The first seeded bulk growth of single crystalline AlN (001) platelets was achieved on 6H–SiC (0001) substrates in the temperature range of 1950–2250°C at 500 torr of N<sub>2</sub>. Optimized sourceto-substrate distances and temperature gradients were crucial for the achievement of these

results. Color variations in the grown crystals were observed above 2150 C and linked to the incorporation of Si and C from the substrate and the growth crucible. The results of comparative SIMS analysis revealed significantly lower levels of Si and C in transparent crystals obtained below 2000 °C. Cracks were observed in all crystals after cooling regardless of the growth temperature. The results of TEM and XRD analyses revealed the absence of line and planar defects and residual stress in the grown crystals. No misoriented grains or twinned regions were observed. The SAD patterns consisted of well defined and sharp diffraction spots representing the 2H AlN crystal structure. Atomic force microscopy images revealed very smooth surfaces (average RMS = 6 Å) on the crystals.

# Acknowledgements

The authors acknowledge the support of the Office of Naval Research under the contract N00014-92-J-1477, Mr. M Rafaniello and the Dow Chemical Company for providing hot-pressed AlN, and Mr. M. McClure and M. Bremser of NCSU for assistance in XPS and AFM studies, respectively.

#### References

- [1] G.A. Slack, T.F. McNelly, J. Crystal Growth 34 (1976) 263.
- [2] G.R. Kline, K.M. Lakin, Proc. IEEE Symp. Ultrasonics 14 (1983) 340.
- [3] M.T. Duffy, in: G.W. Cullen, C.C. Wang (Eds.), Heteroepitaxial Semiconductors for Electronic Devices, Springer, Berlin, 1978, pp. 150–181.
- [4] R.F. Davis, Proc. IEEE 79 (1991) 702.
- [5] S. Strite, H. Morkoc, J. Vac. Sci. Technol. B 10 (1992) 1237.
- [6] J.H. Edgar, J. Mater. Res. 7 (1992) 235.
- [7] G.A. Slack, T.F. McNelly, J. Crystal Growth 34 (1976) 263.
- [8] G.A. Slack, T.F. McNelly, J. Crystal Growth 42 (1977) 560.
- [9] W.F. Knippenberg, G. Verspui, US Patent 3.634.149.
- [10] J.O. Huml, G.S. Layne, US. Patent 3.607.014.
- [11] J.O. Huml, G.S. Layne, US. Patent 3.598.526.
- [12] P.M. Dryburgh, J. Crystal Growth 94 (1989) 23.
- [13] R.B. Campbell, H.C. Chang, Technical Report AFAPL-TR-67-23, Westinghouse Electrical Corporation, Pittsburgh, PA, 1967.
- [14] J. Pastrňák, L. Roskovcová, Phys. Stat. Sol. 7 (1964) 331.
- [15] C.O. Dugger, J. Mat. Res. Bull. 9 (1974) 331.
- [16] C.O. Dugger, Air Force Technical Report, AFORL-TR-75-0486. Hanscom AFB, Massachusetts, 1975.
- [17] A.T. Collins, E.C. Lightowlers, P.J. Dean, Phys. Rev. 158 (1960) 883.
- [18] M. Hoch, D. White, Technical Research Report MCC-1023-TR-216, Ohio State University, 1956.
- [19] HSC Chemisrty, Chemical Reaction and Equilibrium Software, Outokumpu Research, Finland, 1993.
- [20] L.H. Dreger, V.V. Dadape, J.L. Magrave, J. Phys. Chem. 66 (1962) 1556.
- [21] L. Bergman, R.J. Nemanich, Annu. Rev. Mater. Sci. 26 (1996) 551.