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RESEARCH ON ALUMINUM NITRIDE MATERIALS

G. A. Slack and T. F. McNelly

FINAL TECHNICAL REPORT

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This report summarizes the progress made during the second year of AFOSR contract support in growing single crystals and producing ceramic samples of aluminum nitride for use as electronic heat sinks and surface acoustic wave (SAW) devices. An improved aluminum pellet-drop technique for making 70-g quantities of AlN starting material has been developed. By subliming and recondensing this material in sealed tungsten crucibles at temperatures between 2100°C and 2350°C, crystals up to 1.2 cm in length and → over

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ALN

0.4 cm in diameter have been grown. The problem of pinhole attack of tungsten by AlN has been studied in detail, and a technique for producing long-lived crucibles using W foil has been developed. Crystals with a thermal conductivity of at least 2.53 W/cm $^{\circ}$K at 301°K and an electrical resistivity $>10^{13}$ Ω-cm have been grown. Optical absorption and piezoelectric measurements have also been made.

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SUMMARY OF RESULTS

1. Developed an improved aluminum pellet-drop technique for making high purity polycrystalline aluminum nitride ($\mathrm{A}\ell\mathrm{N}$) in 70-gram quantities.
2. Produced and characterized an $\mathrm{A}\ell\mathrm{N}$ ceramic bonded with less than 1 weight percent aluminum.
3. Devised a sublimation-recondensation technique that produces polycrystalline $\mathrm{A}\ell\mathrm{N}$ without unreacted aluminum.
4. Studied the attack of several types of tungsten and tungsten-rhenium alloy crucibles by $\mathrm{A}\ell\mathrm{N}$ at high temperatures.
5. Devised a method of making long-lived crucibles from tungsten foil.
6. Grown a variety of $\mathrm{A}\ell\mathrm{N}$ crystals.
7. Studied $\mathrm{A}\ell\mathrm{N}$ growth morphology versus temperature.
8. Measured 2.53 W/cm ^{o}K at 301^{o}K as the thermal conductivity of single-crystal $\mathrm{A}\ell\mathrm{N}$ from run W-154.
9. Made optical absorption, electrical resistivity, and piezoelectric measurements on several $\mathrm{A}\ell\mathrm{N}$ crystals.

Section 1

INTRODUCTION

The main limitation on power handling by semiconductor devices is the extraction of heat generated during their operation. The substrate which is bonded to the active semiconductor must transmit this heat with minimal temperature rise and must match the thermal expansion of the semiconductor well in order to prevent strain damage. Usually high electrical resistivity is also required. Other than synthetic diamond, which is expensive, the only reasonable material that would extend the state-of-the-art is aluminum nitride. Pure $A\ell N$ has a thermal conductivity about 80 percent that of copper, an electrical resistivity over 10^{14} Ω-cm, and a thermal expansion that closely matches silicon. A review of the problems of growing suitable, high-purity $A\ell N$ crystals and a brief discussion of the known properties have been written (Ref. 1) by the principal investigators and should be referred to for details.

The electrical and thermal conductivities of $A\ell N$ are both strongly influenced by impurities. For the thermal conductivity, K, oxygen is usually the most troublesome impurity. An oxygen content of about 275 ppm will reduce K by about 10 percent (Ref. 2). This report describes the growth of crystals with a K of at least 2.53 W/cm $^{\circ}$K, within 80 percent of the maximum predicted value (Ref. 2).

In order to make usable $A\ell N$ heat sinks, one can either make fine-grained polycrystalline ceramic or single crystals. The better candidate for good heat sinks is single-crystal material. Single-crystal $A\ell N$ is a promising material for surface acoustic wave (SAW) devices. It has a high piezoelectric coupling coefficient and a high surface wave velocity. The size and perfection of crystals needed for this application are somewhat greater than that for heat sinks.

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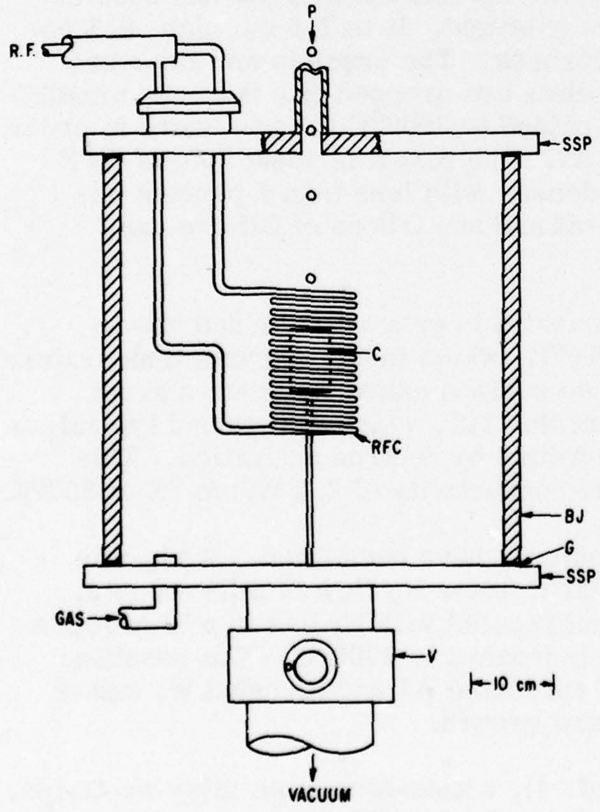
Section 2

PROGRESS DURING SECOND YEAR

PRODUCTION OF STARTING MATERIAL

The production of high-purity starting material is one of the critical problems in the growth of AℓN single crystals. The aluminum pellet-drop technique described in detail in the First Annual Technical Report (Ref. 3) is depicted in Figure 1. Though tedious, the process works well. Several improvements have been made in the last year. A 0.04-cm thick pyrolytic boron nitride liner has been placed inside the tungsten crucible, as shown in Figure 2. The W is used only as a susceptor. The Aℓ pellets do not noticeably attack the BN, but react with the surrounding N_2 gas to form AℓN. In the previous method, the molten Aℓ attacked the W crucible, and the AℓN charge was contaminated with up to 0.5 weight percent W. This problem is now avoided. In the present method, pellets are sheared from high-purity, zone-refined Aℓ rod. The pellets now used weigh 0.06 g, five times less than previously, thus they react more completely.



BJ	cylindrical glass bell jar
C	tungsten crucible
G	viton rubber gasket
GAS	95% N_2 + 5% H_2 gas
P	high-purity aluminum pellet
RF	RF power supply
RFC	RF heating coil, water-cooled copper
SSP	stainless steel plate
V	large-aperture gate valve

Figure 1. Pellet-drop Furnace for Making High-purity AℓN

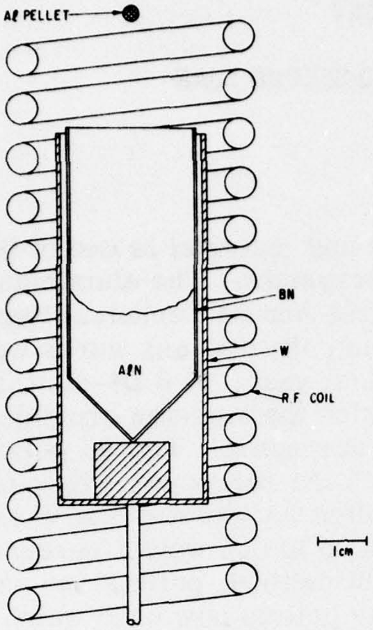


Figure 2.
Crucible Arrangement for Pellet-drop Furnace

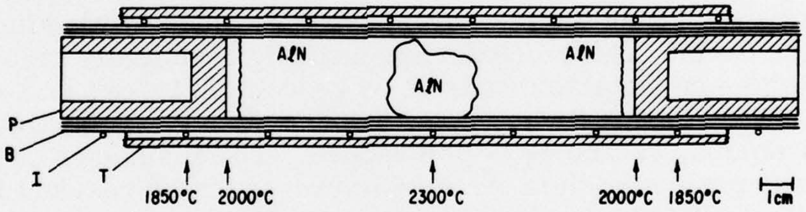
So that more material can be prepared during a run, a method of reloading the pellet supply without allowing air into the bell jar has been devised. The W crucible has also been enlarged. It is 7.5 cm high, 2.5 cm in diameter, with a 0.09 cm wall thickness. The crucible and liner are heated to 1850^{o}C and about 750 Aℓ pellets are dropped into it at one minute intervals. The temperature is then raised to 2000^{o}C for two hours in order to diminish the amount of unreacted Aℓ. The result is about 70 g of AℓN with about 85 percent of theoretical density with less than 1 percent unreacted Aℓ. The BN liner is peeled off and any traces of BN are sand blasted away.

Because of unreacted Aℓ, the material is gray in color and has an electrical resistivity of 1 Ω-cm at 300^{o}K, which increases with temperature. The material has low surface area, so surface oxidation is not a great problem. Aluminum nitride from run No. 101, which is believed typical, had an oxygen content of 450 ppm by weight by neutron activation. This AℓN was measured to have a thermal conductivity of 2.2 W/cm ^{o}K at 300^{o}K.

Several other AℓN production methods have been tried. WAl_4 was prepared by reacting Aℓ and W at 1500^{o}C under H_2 flow in a RF-heated, cold copper boat. The WAl_4 was then reacted with N_2 gas in a W crucible at temperatures that were gradually increased to 2000^{o}C. The resulting material contained large amounts of unreacted Aℓ and included W, and is not a good starting material for crystal growth.

Following an idea by Philips (Ref. 4), a zinc-aluminum alloy was tried. An alloy containing equal parts by weight of Aℓ and Zn was made and then reacted with N_2 at temperatures gradually increased to 2000°C. During this process the zinc evaporates creating a porosity that enables essentially complete nitriding of the Aℓ. The residual zinc content was measured as 30 ppm by weight. However, this AℓN material has a high surface area and will quickly develop a high oxygen content through surface oxidation if exposured to room air. For this reason the pellet-drop technique is preferred.

The ceramic AℓN from the pellet-drop process contains a few tenths of a percent excess Aℓ. The most satisfactory way to nitride the excess Aℓ is to sublime and recondense it in an atmosphere of high-purity N_2. The setup used is shown in Figure 3. The ceramic is placed in the center of a roll of 1-mil W foil. The ends of the roll are plugged with W slugs, and the roll is kept from unwinding with W wires. The roll is placed in a high-purity N_2 environment and RF heated either directly or via a W susceptor tube. For a 30-g charge heated to 2300°C, 1 g/h to 3 g/h sublime and then recondense on the end plugs which are held at about 2000°C. The deposit is a dark amber mass of fully dense AℓN crystals, as shown on the left in Figure 4. The plug on the right in Figure 4 was held at 1920°C. The deposit on it is a lighter colored dense mass of whiskers. The deposits have electrical resistivities of over 10^{13} Ω-cm and, thus, contain no detectable free Aℓ. Sufficient N_2 gas flows in around the foil spiral, or diffuses through it, to complete the nitriding. Surprisingly no noticeable Aℓ vapor leaks out. This point is discussed in the next section.



B tungsten foil blanket roll
I tungsten wire wrapping
P solid tungsten plug
T tungsten susceptor tube

Figure 3. Sublimation Insert for Furnace in Figure 9

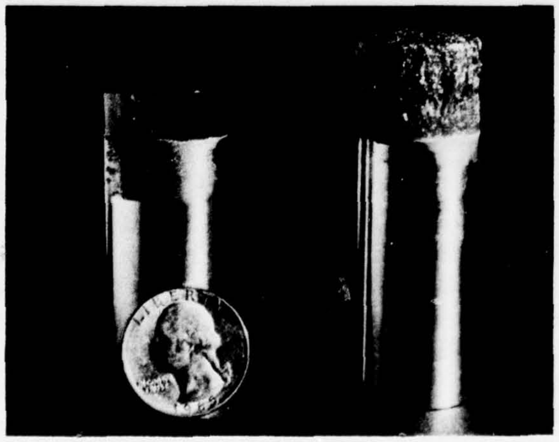


Figure 4.

Polycrystalline AℓN Grown in Furnace Shown in Figure 3

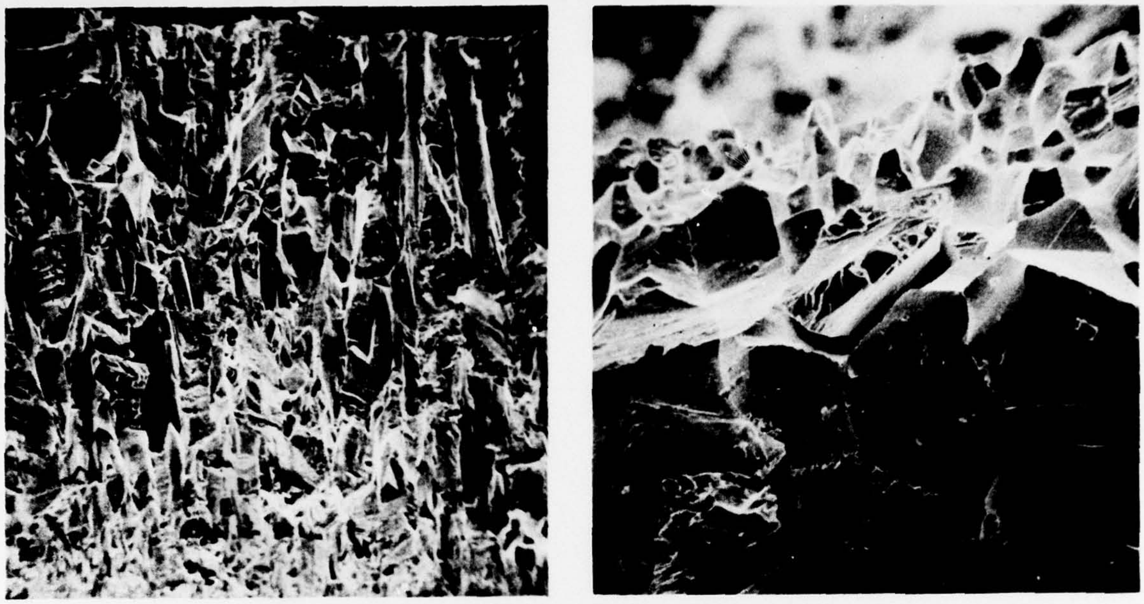
CRUCIBLES

The most severe problem encountered in growing AℓN crystals has been the construction of suitable crucibles. Tungsten in contact with AℓN under one atmosphere of nitrogen pressure forms a liquid phase with the release of nitrogen gas at about 2450°C. At lower temperatures, W grain boundaries are gradually attacked by AℓN. As shown in Figures 5c and 5d, the attack begins with the formation of bubbles along the grain boundaries; these grow and eventually coalesce into channels, often with a series of parallel side channels. The channels form first along the lines where three grains intersect, but in severely attacked tungsten they are present at perhaps 0.1-mm intervals all along the surface of each W grain. Such a crucible typically leaks several tenths of a gram of AℓN an hour, rendering it useless for crystal growing.

Initially, it was thought this attack was caused by residual oxygen impurities in the AℓN. Oxygen would diffuse through the W then sublime away as a tungsten oxide. However, subsequent experiments have shown that attack does not occur for crucibles containing $A\ell_2O_3$ and that mixtures of AℓN + $A\ell_2O_3$ or AℓN with large quantities of oxygen in solid solution (to at least 0.3 atom percent) are attacked no differently than with high-purity AℓN.

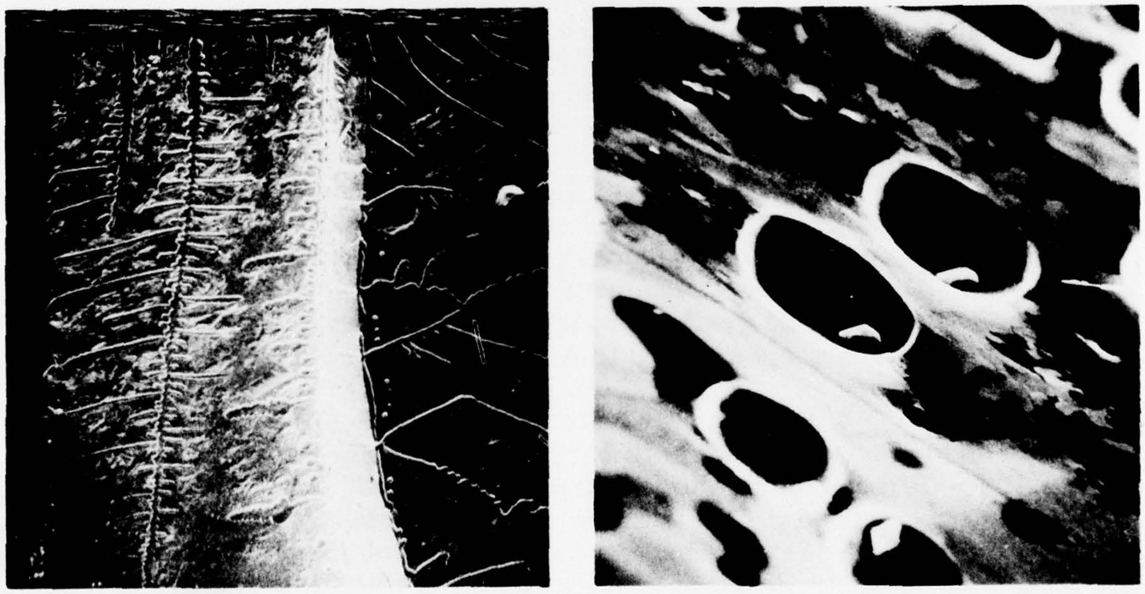
The next conjecture was that residual gas atoms entrapped in the W were migrating at high temperatures, possibly aided by aluminum, to produce the leaks. The crucibles are made by chemically vapor depositing (CVD) tungsten on suitable mandrels by reducing WF_6 or, less commonly, $WC\ell_6$ with H_2. During the process, halogen atoms and, particularly at the grain boundaries, vacancies are entrapped. The resistance of the W to high-temperature grain growth is strongly improved by the residual fluorine content, thus CVD W from the fluoride process is usually made to contain 10 ppm to 20 ppm F by weight (Ref. 5). Material with higher fluorine concentrations is known to form many bubbles at high temperatures. The Chemetal Corporation, however, uses a process of adding water or oxygen to the gas stream that produces a grain growth-resistant microstructure with 1 ppm to 2 ppm F and 5 ppm to 20 ppm O by weight (Ref. 6).

Fluoride CVD W crucibles (both normal and low fluorine concentration, with wall thicknesses from 0.38 mm to 1.2 mm) from three different suppliers, have been used. An attempt was made to bake crucibles at 2600°C in vacuum to reduce trapped halogen and voids. Figure 6 summarizes the findings. Crucible lifetime is nearly a week at 2100°C, but roughly halves with every 50°C of temperature increase. This is approximately the same temperature rise that doubles the aluminum vapor pressure in equilibrium with AℓN at one atmosphere of nitrogen. This implies that Aℓ vapor is the controlling factor in pinhole formation.



(a) Virgin WF_6 CVD crucible, note columnar grains (200X)

(b) Virgin $WC\ell_6$ CVD crucible, note more uniaxed grains (200X)



(c) $WC\ell_6$ CVD crucible after $A\ell N$ run of 31 hours at $2310^{\circ}C$, note large grains with channels and tributaries (160X)

(d) WF_6 CVD crucible after $A\ell N$ run, crystals in internal voids are $A\ell F_3$ (5000X)

Figure 5. Scanning Electron Micrographs of Grain Structure of CVD W Crucibles

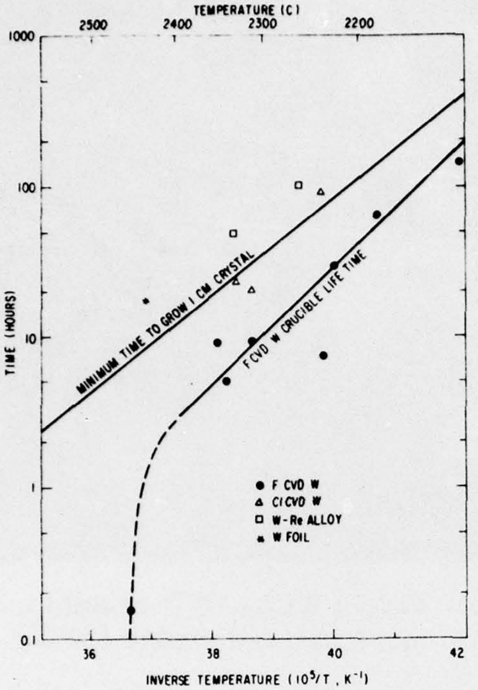


Figure 6.

Comparison of Lifetime of Sealed Crucibles Containing $A\ell N$ and Time Required to Grow a 1-cm Crystal

Fluorine is involved in the process, however. The scanning electron micrograph in Figure 5d shows voids that have formed at an internal grain boundary during the course of a growth run. The micrometer-sized crystals in the voids were removed, x-rayed, and identified as $A\ell F_3$. At $A\ell N$ growth temperatures, these crystals would vaporize and fill the cavities with many atmospheres of $A\ell F_3$ gas (Ref. 7). It was thought that this pressure might provide the driving force for pinhole formation. Baking the F CVD crucibles at 2600^{o}C in vacuum removes all of the trapped fluorine, but only slightly increases the useful life of the crucibles for $A\ell N$ growth. Pinholes still form at the grain boundaries. Thus, pinhole formation can occur without fluorine and appears to be intrinsic to the $A\ell N$-W system.

Chloride CVD W is somewhat better, probably due to its microstructure. Fluoride process W tends to have columnar grains, with the long axis $< 100 >$, aligned normal to the crucible surface. Chloride process W tends to more equiaxed grains with the $< 111 >$ normal to the surface (Ref. 8) (see Figures 5a and 5b). Because of the columnar structure, paths from inside to outside along the grain boundaries tend to be more direct and shorter in F CVD W. Pinholes form in $C\ell$ CVD, but require around three times longer. The high-temperature bake-out of an empty crucible to remove halogen actually decreases the useful life of $C\ell$ CVD W. At 2600^{o}C, grains rapidly grow to 5 mm in diameter with a thickness equal to the wall thickness. Thus, a single-grain boundary extends completely through the crucible wall, more or less perpendicular to the surface. Pinholes form at the inner wall and eat their way directly to the outside.

Eighty five percent W, 15 percent Re alloy F process CVD crucibles have been used in hopes of reducing grain growth and preventing cracking caused by tension on the AℓN due to differential thermal expansion between the crystal and the crucible. Grain growth is slower, and the lifetime is slightly better than with Cℓ CVD W, as shown in Figure 6.

The longest lived crucibles we have constructed are made by tightly rolling 1-mil W foil around two solid W end plugs. The AℓN change is placed in the center, and the roll is held together with W wire on the outside, as shown in Figure 3. When the center is RF heated, directly or with a susceptor tube, AℓN sublimes and recondenses on the end plugs which are held at a lower temperature. Aluminum and N_2 vapor penetrate the gap between the plugs and the roll of foil until the temperature has dropped to 1850°C. A hermetic seal is quickly formed here by condensed AℓN with no noticeable AℓN loss. Surprisingly, Aℓ vapor does not leak out through the spiral sides of the foil. The flow impedance of a tight roll is quite high, for N_2 gas in our geometry and growth conditions perhaps 10^{-6} atm-l/s. The leak rate of Aℓ is probably much less. Aluminum vapor sticks readily to W, and probably Aℓ vapor only traverses the spiral by a slow hopping process. The foil is subject to pinhole attack, but each foil layer must be holed sequentially. As shown in Figure 6, a seven-layer roll lasted approximately seven times the expected life of a F CVD W crucible. Rolls with still more layers are being tried. An experiment is underway to rhenium braze the W end plugs to the roll so that they can be run at a higher temperature for better control of nucleation.

Graphed in Figure 7 is the measured growth rate of AℓN versus the source temperature. The data has been corrected for resublimation from the growing crystal; thus, this is the rate of growth on a very cold substrate. The measured growth rate agrees with a theory that assumes: 1) N_2 pressure is one atmosphere, 2) Aℓ pressure is in equilibrium with AℓN at the source, 3) vapor transport is not the rate limiting step, 4) Aℓ sticking coefficient is near unity, and 5) a N_2 molecule sticks to the growing crystal only every 3×10^4 collisions. This low sticking coefficient is to be expected because of the extremely high binding energy of the N_2 molecule, 9.77 eV (Ref. 9).

The minimum time to grow a 1-cm crystal is compared with the crucible lifetime in Figure 6. The increase in crystal growth rate at higher temperatures is almost exactly compensated by the decrease in crucible life. Thus, the size of a crystal that can be grown before leakage starts is nearly independent of temperature. For practical crystal growth, longer times than shown are required to allow control of nucleation and to allow some resublimation. Therefore, growth of centimeter size crystals with single-layer W crucibles is marginal. Multilayer foil crucibles seem promising, however.

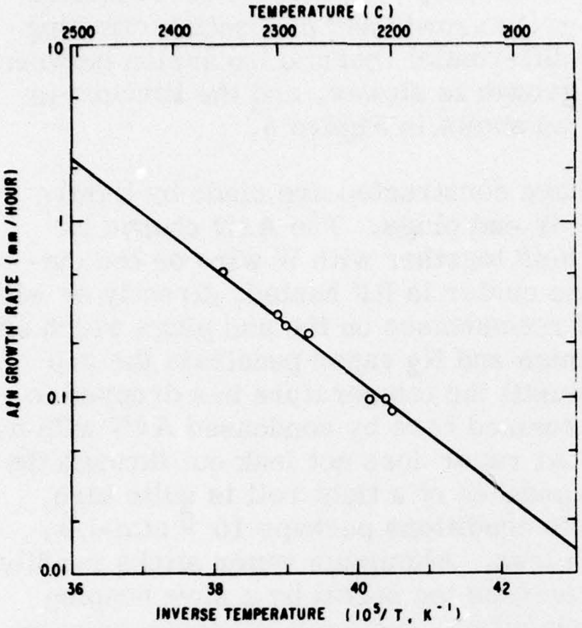


Figure 7.

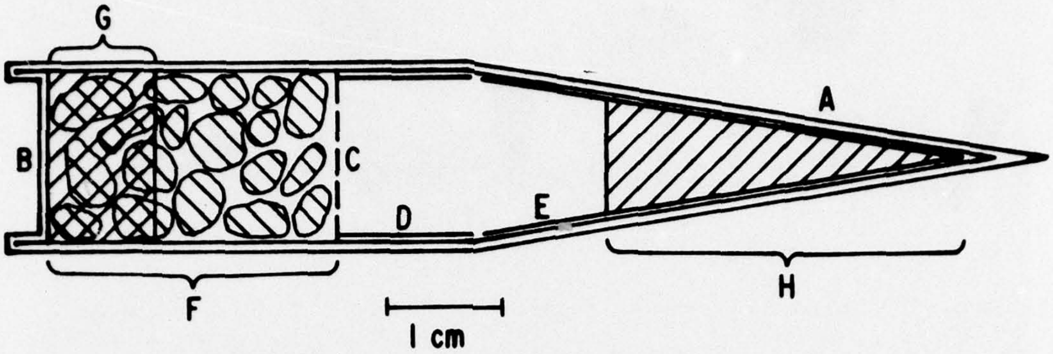
Growth Rate of AℓN in Sealed Crucibles vs Source Temperature, Corrected for Resublimation During Growth

We have experimented with other crucible materials. There are six elements with melting points over 2500°C: Mo, Os, Ta, Re, W, and C. Carbon badly dopes AℓN. Molybdenum reacts too readily with Aℓ, and Ta too readily with N. The Os-Aℓ phase diagram has not been determined, and Os is quite expensive and toxic. We have found that Re forms a liquid phase with AℓN at around 2400°C. We are now investigating whether grain boundary attack is a problem with Re at lower temperature. We have found that ZrN and Ta_2N are not sufficiently stable for crucibles. We are currently evaluating HfB_2 and ZrB_2.

CRYSTAL GROWTH

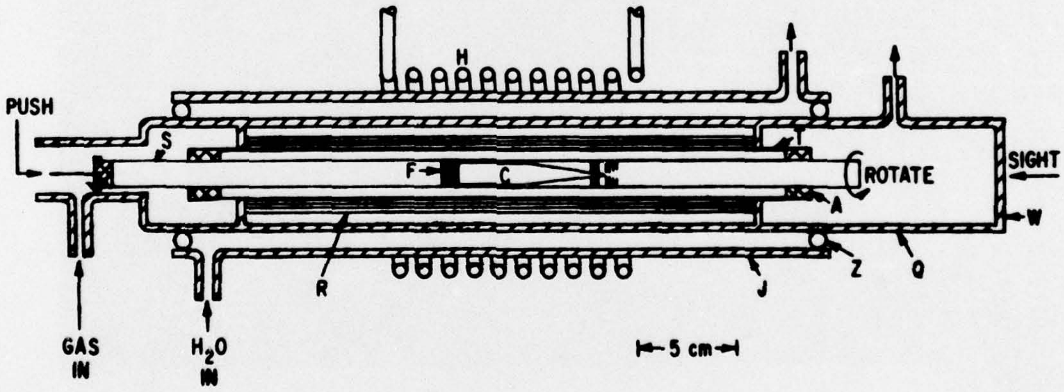
In most growth experiments, CVD W crucibles were loaded as shown in Figure 8. The Re liner was not always used. Crucibles were loaded into the furnace, depicted in Figure 9, and pushed slowly through an RF coil. In some runs the crucible was also rotated. A detailed description of the furnace and the growth sequence can be found in the First Annual Technical Report (Ref. 3). Crystals have been grown with push rates between 0 and 0.9 mm/h; the maximum susceptor temperatures ranged from 2100°C to 2350°C.

As described in the previous section, crucible failure has placed severe restrictions on crystal growth. Figures 10 and 11 display the results of eight growth runs. Except for runs W-156 and W-158, growth was continued until leakage occurred. The end faces of the conical boules are basically discs in runs W-154 and W-180, implying that the isotherms are planes normal to the cone axis. The other runs have concave boule ends. This



A	CVD tungsten crucible, wall thickness: 0.075 cm
B	CVD tungsten cap welded shut
C	perforated tungsten foil charge holder
D	tungsten spacer
E	Re liner
F	initial AℓN charge
G	AℓN regrown on cap
H	final AℓN crystal regrown in tip

Figure 8. Crucible Arrangement for Growing AℓN Crystals



A	$A\ell_2O_3$ ceramic	R	rolled foil radiation shield
C	W crucible	S	W support tube
F	flat foil W radiation shields	T	W susceptor tube
H	RF heating coil	W	clear fused quartz window
J	water cooling jacket	Z	rubber O-ring seal
Q	fused quartz housing		

Figure 9. Tungsten Tube Furnace for Growing AℓN Crystals

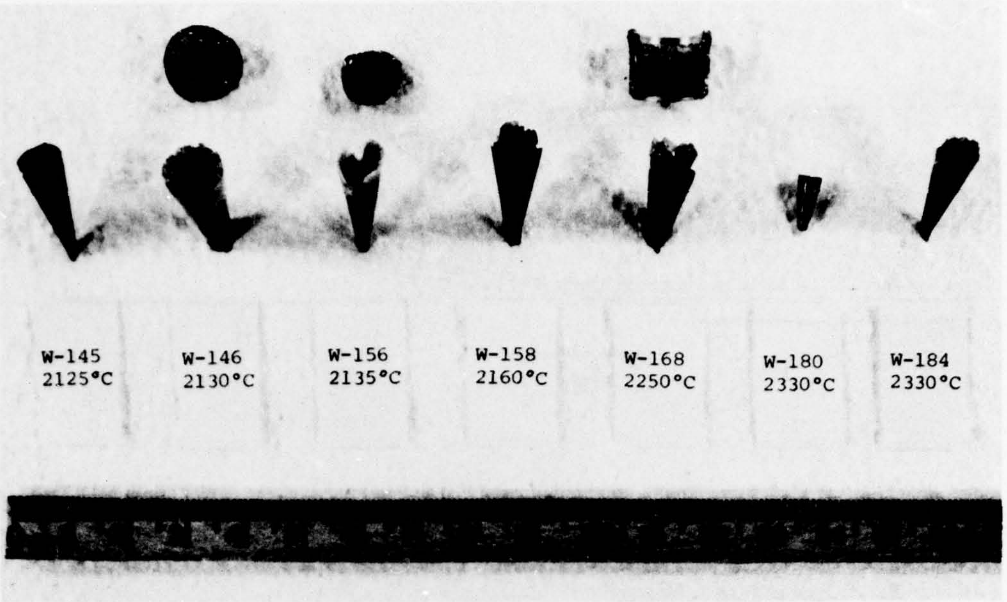


Figure 10. AℓN Crystals Grown During Seven Runs. At top are residues of starting charges.

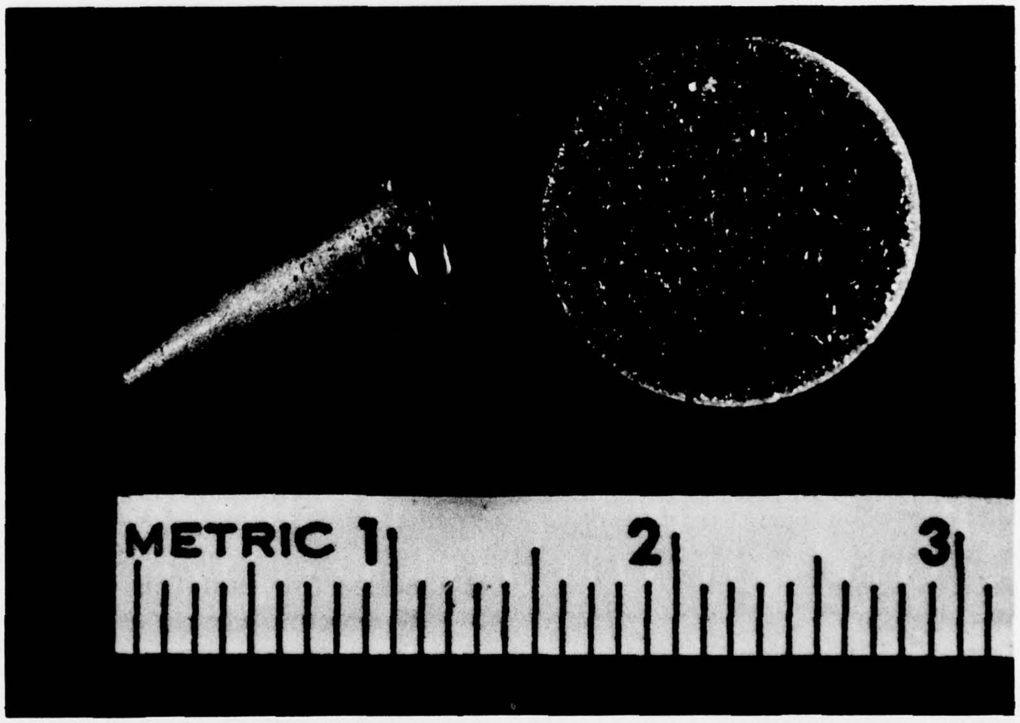


Figure 11. Aluminum Nitride Boule from Run No. W-154 (left). Approximately 90 percent of cone is a single crystal. On right is residue of polycrystalline starting charge.

probably does not imply that the isotherms in these cases were concave, rather the crucibles were pushed faster than the intrinsic crystal growth rate. The maximum possible rate of crystal growth varies during the run and is not equal to the rate of sublimation of the charge, due to the changing cross-sectional area of the crucible. Therefore, for the most efficient crystal growth the push rate must be varied during the run in a complicated fashion depending on: the temperature profile of the furnace, the growth rate of AℓN versus the temperature, and the predicted lifetime of the crucible. If crucible life was not such a serious constraint, the push rate could be small and constant, and these difficulties avoided. The runs with hollow growth have nucleated additional crystallites on the walls. Run W-154 is nearly all a single crystal, and run W-180 contains large crystallites.

Several experiments were carried out to try to increase the AℓN growth rate without increasing the temperature. A small amount of Ta_2N, Mn, and CaF, respectively, were added to the AℓN in three different runs. Since Ta, Mn, and Ca form fairly stable nitrides, it was hoped they might catalyze the splitting of the N_2 molecule. However, none of them significantly changed the growth rate.

The growth habit of AℓN has been studied. At temperatures less than 2000°C, AℓN tends to grow as needles with the C-axis long. At higher temperatures, the needles tend to fuse into plates with $(\bar{1}120)$ faces. Hexagonal columns and more equiaxed crystals are found at still higher temperatures. Growth tends to be nearly along either direction of the C-axis. Cleavage has been observed normal to $\langle \bar{1}100 \rangle$ and $\langle 0001 \rangle$.

OPTICAL ABSORPTION AND OTHER PROPERTIES

A discussion of impurity-induced optical absorption in AℓN was included in the First Annual Technical Report (Ref. 3). Figure 12 displays the absorption for a variety of AℓN crystals. The P&R curve is the data of Pastrnak and Roskovcova (Ref. 10) for a crystal with considerable (about 5000 ppm) oxygen. The Air Force Cambridge Research Laboratories crystal was grown in graphite and contains carbon as an impurity (Ref. 11). The other crystals were grown at General Electric Corporate Research and Development in sealed W crucibles. As described in the last report, the absorption at 15 000 cm^{-1} is probably due to C, that at 32 000 cm^{-1} and 45 000 cm^{-1} due to O, and that 22,500 cm^{-1} due to N vacancies. Crystal W-154 shows the lowest overall impurity absorption of any sample yet studied.

Figure 13 shows the spectrum of two separate regions of boule W-154 that grew as twins with their C-axes along the growth direction but antiparallel. The twin which has the Aℓ face toward the incoming gas has an absorption coefficient, α, of about 20 cm^{-1} from 21 000 to 46 000 wave numbers. The antiparallel twin with the N face toward the incoming gas has α

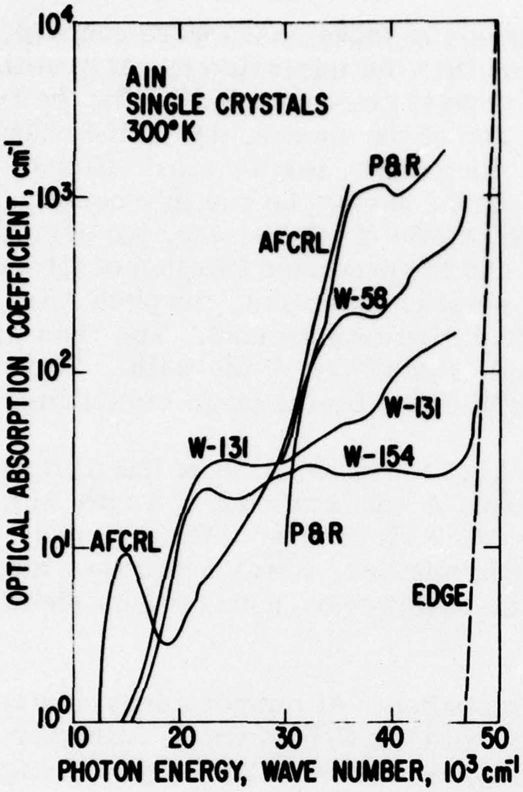


Figure 12.

Optical Absorption Coefficient vs Photon Wave Number for Several Single Crystals of AℓN

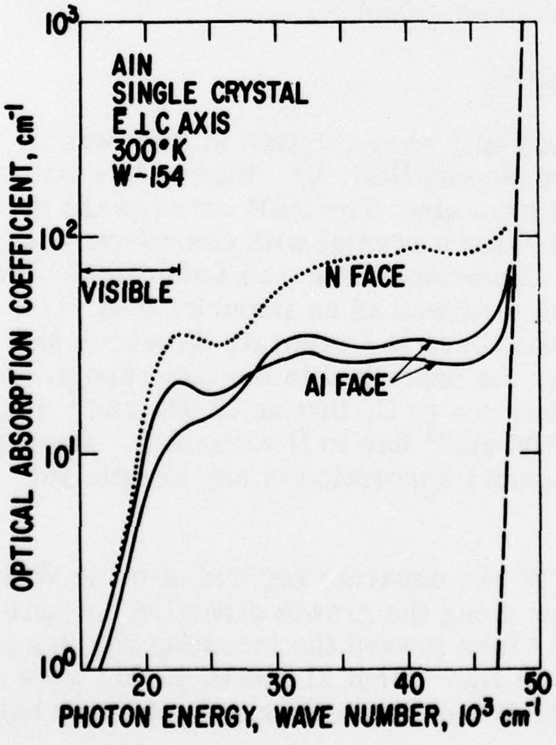


Figure 13.

Optical Absorption Coefficient vs Photon Wave Number for Crystal W-154 of AℓN about 60 cm^{-1}. Thus, the N face, during growth, picks up more impurities and/or N vacancies. The face identifications were made from the sign of the piezoelectric voltage developed under static stress in analogy with BeO, ZnS, CdS, and CdSe.

Samples of this crystal were sent to Dr. Paul Carr of AFCRL for additional piezoelectric and acoustic measurements. Unfortunately, the samples have proved to be too small for such measurements. Samples were also sent to Dr. Richard Forman of the National Bureau of Standards, Gaithersburg, Md for studies of low-temperature optical properties. He finds that there is no great change in the absorption as the temperature is lowered to $4^{o}K$. The thermal conductivity of this crystal has been measured as 2.53 $W/cm^{o}K$ at $301^{o}K$. The sample has a small crack so the thermal conductivity may be even higher. The electrical conductivity of the sample is less than $10^{-13}\ \Omega^{-1}\ cm^{-1}$.

Section 3

PERSONNEL, PUBLICATIONS, AND TALKS

PROJECT PERSONNEL

Dr. Glen A. Slack
Dr. Thomas F. McNelly
Warren S. Knapp

PUBLICATIONS

Two papers were published during the second year of the contract. The first covers work on AℓN funded by General Electric Corporate Research and Development done prior to AFOSR support. The second covers work done under AFOSR support and is included as an appendix to this report.

G. A. Slack and T. F. McNelly, "Growth of High Purity Aluminum Nitride Crystals," Journal of Crystal Growth, Vol. 34, 1976, pp. 263-79.

G. A. Slack and T. F. McNelly, "AℓN Single Crystals," Journal of Crystal Growth, Vol. 42, 1977, pp. 560-3.

CONFERENCE TALKS

A paper entitled AℓN Single Crystals, by G. A. Slack and T. F. McNelly was delivered at the Fifth International Conference on Crystal Growth in Cambridge, Mass., July 19, 1977.

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Section 4

REFERENCES

1. G.A. Slack and T.F. McNelly, "Growth of High Purity AℓN Crystals," Journal of Crystal Growth, Vol. 34, 1976, pp. 263-79.

2. G.A. Slack, "Nonmetallic Crystals with High Thermal Conductivity," Journal of Physics and Chemistry of Solids, Vol. 34, 1973, p. 321.

3. G.A. Slack and T.F. McNelly, Research on Aluminum Nitride Materials, First Annual Technical Report, prepared for Directorate of Electronic and Solid State Science, Air Force Office of Scientific Research, Contract No. F44620-76-C-0039, Corporate Research and Development, General Electric Company, Schenectady, New York, 1976, p. 22.

4. N.V. Philips, Netherlands Patent No. 6 602 899, September 12, 1966.

5. W.A. Bryant, "High-temperature Strength Stability of Three Forms of Chemically Vapor Deposited Tungsten," Journal of Vacuum Science and Technology, Vol. 11, 1974, pp. 695-699.

6. R.A. Holtz, U.S. Patent No. 3 565 676, 1968.

7. J.P. Millet, H. Pham, and M. Rolin, "Phase Diagrams of the Binary Systems Na CL-AℓF_3 and CaF-AℓF_3. Extrapolation of the Triple Point of Aluminum Fluoride," Revue Internationale des Hautes Temperatures et des Refractaires, Vol. 11, 1974, p. 277.

8. W.R. Holman and F.J. Huegel, "Interrelationships Between Process Parameters, Structure and Properties of CVD Tungsten and Tungsten-Rhenium Alloys," Journal of Vacuum Science and Technology, Vol. 11, 1974, pp. 701-708.

9. G.E. Moore and H.H. Hansen, "Direct Observation of the Thermal Dissociation of Molecular Nitrogen," Journal of Chemical Physics, Vol. 54, 1971, p. 399.

10. J. Pastrnak and L. Roskovcova, "Optical Absorption Edge of AℓN Single Crystals," Physica Status Solidi, Vol. 26, 1968, p. 591.

11. A. Armington, private communication.

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Journal of Crystal Growth 42 (1977) 560–563

AlN SINGLE CRYSTALS *

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Single crystals of aluminum nitride up to 1 cm long and 0.3 in diameter have been grown by a sublimation–recondensation technique at about 2250°C. The starting material is prepared by the direct reaction of aluminum and nitrogen at 1850°C. The crystals are grown at a rate of 0.03 cm/hr. in sealed tungsten crucibes in an rf heated tungsten furnace. They are amber in color and have the wurtzite structure.

1. Introduction

The fundamental problems encountered in growing high purity crystals of AlN have been treated previously [1]. The present work describes some advances made since then. These advances have been in the size of the crystals grown and in their purity.

2. Starting material

The first advance has been the development of a new method to make higher purity AlN starting material for the subsequent crystal growth. The method is called the pellet-drop technique and is illustrated in fig. 1. Cylindrical pellets of Al metal 0.32 cm in diameter and 0.32 cm long of mass 0.07 gm each are dropped, at one-minute intervals, into a hot crucible. The crucible is surrounded by a high-purity gas mixture of 95% N_2 + 5% H_2 at one atmosphere pressure. The molten aluminum reacts with the nitrogen to form AlN. The crucible is heated by a radio-frequency coil operating at 0.5 megacycles, and is held at about 1850°C. The crucible arrangement is shown in fig. 2. The outer tungsten crucible, made by chemical-vapor-deposition, is 7.5 cm high,

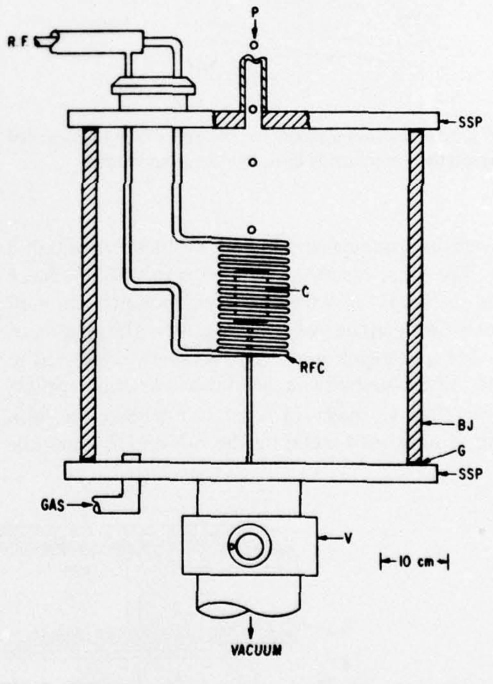

Fig. 1. Pellet-drop furnace for making high-purity AlN: BJ = cylindrical glass bell jar, C = tungsten crucible, G = viton rubber gasket, GAS = 95% N_2 + 5% H_2 gas, P = high-purity aluminum pellet, RF = radio frequency power supply, RFC = rf heating coil, water-cooled copper, SSP = stainless steel plate, V = large aperture gate valve.

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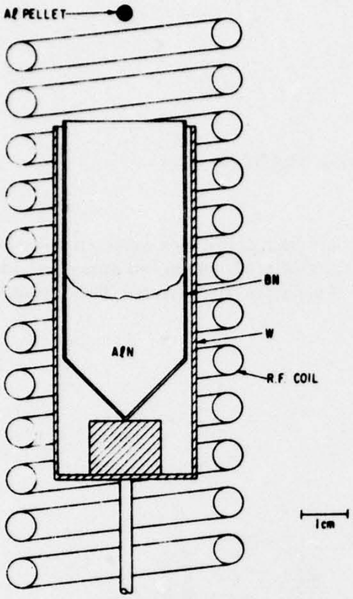

Fig. 2. Crucible arrangement for the pellet-drop furnace: BN = pyrolytic boron nitride liner, W = tungsten crucible.

2.6 cm in diameter, and has a wall thickness of 0.090 cm. The inner crucible, made of pyrolytic BN, has a wall thickness of 0.040 cm. The molten aluminum comes into contact only with the BN. The erosion of the BN is negligible and the Al is rapidly converted to AlN. The aluminum is introduced as small pellets rather than en masse in order to minimize the trapping of unreacted metal by the AlN and to lessen the exposure of the BN crucible to molten aluminum. About 700 pellets are reacted per batch. The resulting charge is a dense, grey ceramic of AlN with about 1% excess Al and a residual oxygen concentration of about 400 ppm by weight.

The BN crucible is mechanically removed from the surface of the AlN charge. The charge is then placed in the center of a tungsten tube furnace shown in fig. 3. The walls of the furnace are made of wrapped 0.003 cm thick tungsten foil, the ends are solid tungsten. The furnace is operated in 95% N_2 + 5% H_2 gas at 1 atm. This gas has easy access to the AlN charge through the layers of foil. The charge of about 70 g is held at 2300°C for 12 to 24 h. At the end of this time the charge has evaporated to the ends of the chamber where it condenses out as AlN at about 2000°C. This sublimation process reduces the excess Al content of the AlN to less than 0.1%. The deposited AlN is a clear, transparent, amber colored polycrystalline mass of nearly theoretical density. This material is now ready to be placed into sealed tungsten crucibles for the final growth process.

3. Crystal growth

The crystal growing furnace is shown in fig. 4. The charge of about 5 g of AlN is placed in the left-hand end of the crucible C. The sharp tip of the crucible is placed in the center of the furnace at the start of the run. It is rotated at about 2 rev/h and pushed through the hot zone at about 0.3 mm/h. The total running time is about 150 h. The center of the furnace is held at 2250°C. This technique is similar to

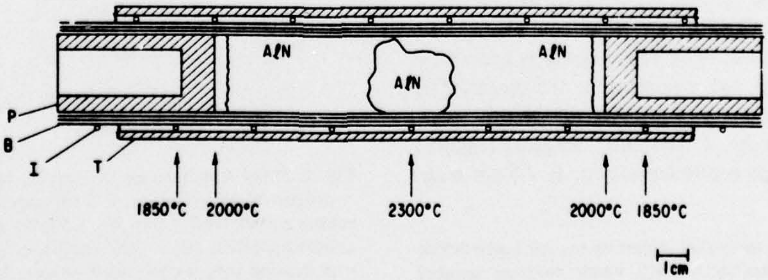

Fig. 3. Sublimation insert for furnace in Fig. 4: B = tungsten foil blanket roll, I = tungsten wire wrapping, P = solid tungsten plug, T = tungsten susceptor tube.

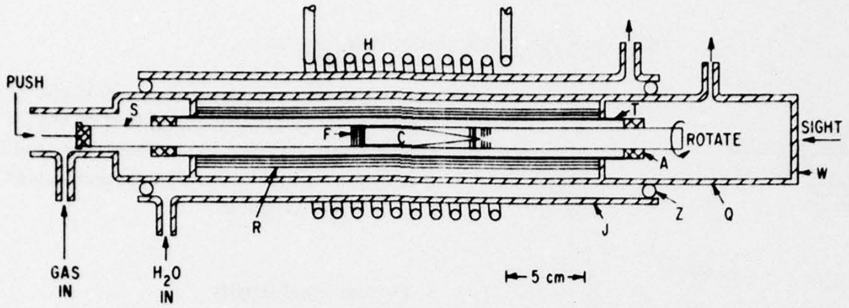

Fig. 4. Tungsten tube furnace for growing AlN crystals: A = aluminum oxide ceramic, C = tungsten crucible, F = flat foil tungsten radiation shields, H = radio frequency heating coil, J = water cooling jacket, Q = fused quartz housing, R = rolled foil radiation shield, S = tungsten support tube, T = tungsten susceptor tube, W = clear fused quartz window, Z = rubber O-ring seal.

the one developed by Piper and Polich [2] for CdS, which grows at a much lower temperature. The largest single crystal of AlN grown with this technique was a conical boule 12 mm long, 4 mm in diameter with a mass of 0.23 g. The c-axis of the AlN crystals are generally parallel to the long dimension of the tungsten crucible. The crystals are amber in color and have the wurtzite structure.

One of the problems that limits the maximum size of the crystals is that the tungsten crucibles tend to develop pin-hole leaks at the grain boundaries after many hours of running time. These pin-holes are about 5 μm in diameter. The CVD crucibles made by the tungsten fluoride process generally have shorter lives than those made by the chloride process. The pin-holes develop faster at higher growth temperatures. If this problem can be solved, then even larger crystals can be grown.

4. Optical properties

The band-gap of AlN is 6.2 eV (50,000 cm^{-1}) according to Yim et al. [3]. Thus there are no intrinsic absorption one-photon processes [1] in the photon wavenumber range $2500 \leqslant \nu \leqslant 50{,}000\ cm^{-1}$. The absorption processes here are believed to be caused by residual impurities or nitrogen vacancies [1]. Fig. 5 shows the optical absorption coefficient data at 300 K on a number of single crystals. The data of Pastrnak and Roskovcova [4] (P & R curve) are for crystals with considerable (about 5000 ppm) amounts of oxygen in them, and represent an average absorption coefficient for the two polarizations. The curves W-58, W-131, and W-154 are for the crystals grown by the present authors, and represent samples of increasing purity. Crystal W-154 probably has about 400 ppm by weight of oxygen. For crystal W-154 the E vector of the light is perpendicular to the c-axis; for the others no special alignment was made. The crystal labelled AFCRL [5] was grown in a graphite furnace

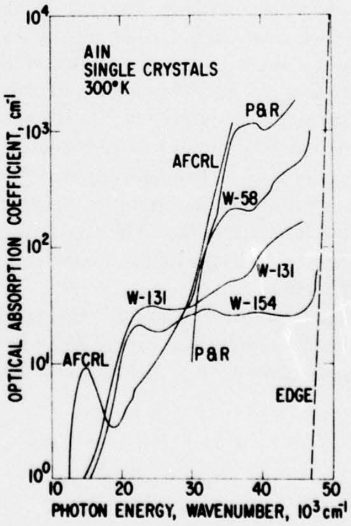

Fig. 5. The optical absorption coefficient versus photon wave-number for several single crystals of AlN.

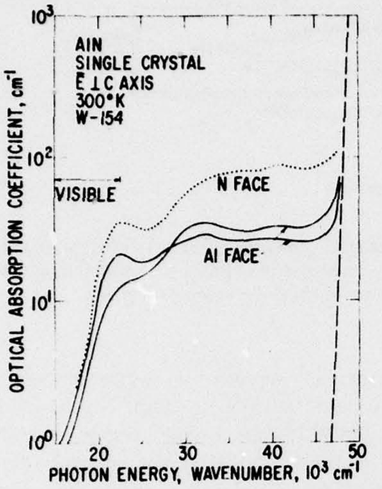

Fig. 6. The optical absorption coefficient versus photon wavenumber for crystal W-154 of AlN.

and presumably contains carbon as an impurity.

Separate portions of boule W-154 were studied more carefully. Separate, twinned sections of the boule grow with their *c*-axes antiparallel. Fig. 6 shows that two regions of a single twin in the crystal which grew with the Al face toward the incoming gas have similar absorption curves with $\alpha \sim 20\ \text{cm}^{-1}$. The antiparallel twin, which had the N face toward the incoming gas, shows $\alpha \sim 60\ \text{cm}^{-1}$. The conclusion is that the N face, during growth, picks up more impurities and/or N vacancies than the Al face. The *c*-axis polarity was determined by the sign of the piezoelectric voltage under static stress.

The identifiable absorption peaks in AlN are $\nu = 15{,}000\ \text{cm}^{-1}$ (carbon impurity), $\nu = 22{,}250\ \text{cm}^{-1}$ (probably nitrogen vacancy), $\nu = 32{,}000$ to $45{,}000\ \text{cm}^{-1}$ (oxygen impurity). Crystal W-154 shows the lowest overall impurity absorption of any of the single or polycrystalline [1] samples yet studied. Further improvement in the crystals should lead to even lower extrinsic α values.

5. Thermal conductivity

The thermal conductivity, K, of an AlN crystal from run W-154 has been measured. The value found was

$$K = 2.5\ \text{W/cm} \cdot \text{deg}$$

at 300 K. A sample of polycrystalline ceramic AlN produced by the pellet-drop technique was measured at 300 K and the value found was

$$K = 2.2\ \text{W/cm} \cdot \text{deg}$$

These values are lower than the theoretical estimate [6] of $K = 3.2$ W/cm deg, but significantly higher than previous reported values [6,7]. The main reason for these higher K values is a reduction in the oxygen impurity content [6].

References

[1] G.A. Slack and T.F. McNelly, J. Crystal Growth 34 (1976) 263.
[2] W.W. Piper and S.J. Polich, J. Appl. Phys. 32 (1961) 1278.
[3] W.M. Yim, E.J. Stofko, P.J. Zanzucchi, J.I. Pankove, M. Ettenberg and S.L. Gilbert, J. Appl. Phys. 44 (1973) 292.
[4] J. Pastrnak and L. Roskovcova, Phys. Status Solidi 26 (1968) 591.
[5] Grown by A. Armington, AFCRL.
[6] G.A. Slack, J. Phys. Chem. Solids 34 (1973) 321.
[7] M.P. Borom, G.A. Slack and J.W. Szymaszek, Bull. Am. Ceram. Soc. 51 (1972) 852.