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GROWTH OF HIGH PURITY AlN CRYSTALS

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The problems associated with the growth of high purity crystals of AlN are reviewed. The impurities Be, C, Mg, Mn, O, S, and Si are discussed. From a review of the literature it appears to be possible to make both n-type and p-type AlN. A technique for producing high purity AlN powder from Al metal by use of AlF_3 as an intermediate product is described. This AlN powder can be converted to single crystals by sublimation in a closed tungsten crucible or in an open tube with a gas flow. Crystals up to a few millimeters in size have been grown.

1. Physical properties of AlN

Aluminum nitride (AlN) is a III–V semiconducting compound. It crystallizes with a wurtzite structure [1], and there are no other polytypes known. According to the periodic table, it is related to two other compounds, BP and SiC. When pure, AlN crystals are hard, colorless, and transparent. The optical bandgap of 6.2 eV [2] involves direct photon transitions at the zone center [3–5]. There is a small variation in the gap with photon polarization [4–6]. A similar anisotropy occurs in GaN [3,4] which also has the wurtzite structure. Other physical properties of AlN, such as thermal expansion [7], refractive index [8], hardness [9–11], sound velocity [12], Young's modulus [13,14], Debye temperature [7], dielectric constant [15,16], hole mobility [17], and photon energies at various critical points in the Brillouin zone [15,16,18,19] have been measured.

2. Chemical properties of AlN

2.1. Dissociation at high temperature

Many chemical properties have also been studied, and some reviews exist [9,20–24]. The melting point of AlN has been the subject of some controversy [25–30], but the most extensive work [29] indicates that at 100 atm pressure of N_2 the first liquid phase occurs at 2800°C. It is probably at this temperature that AlN decomposes into liquid aluminum saturated with nitrogen and into N_2 gas. This may be a peritectic decomposition similar to that found in SiC at 2830°C [31].

The pressure of N_2 gas over solid AlN in equilibrium with liquid Al may be calculated from available thermodynamic data [32]. The vapor over AlN consists of only Al(g) and N_2(g); no AlN molecules exist. The reaction of liquid Al with N_2 has a negative

$$\mathrm{Al\,(l)} + \tfrac{1}{2}\,\mathrm{N_2\,(g)} \rightarrow \mathrm{AlN\,(s)} \qquad (1)$$

free energy change for all temperatures below 2563°C. The pressure of $N_2(g)$ necessary to react with Al(l) to form AlN is 1 atm at 2563°C. At all lower temperatures it is less. The value of $P(N_2)$ in equilibrium with the two-phase system $Al(l)$ and AlN(s) as calculated from the JANAF data [32] is labeled $P_0(N_2)$. If, for the given temperature, the N_2 pressure exceeds the value given, AlN is the only condensed phase present; if it is less, only liquid Al is present. The curve of $P_0(N_2)$ versus T^{-1} is plotted in fig. 1. This calculated pressure is 1, 10 or 100 atm at 2563, 2815, or 3117°C, respectively, as shown in table 1. The pressure of aluminum vapor over the aluminum liquid in eq. (1) is assumed to be the same as that over pure liquid aluminum. This assumption is valid if the solubility of nitrogen in liquid aluminum is very small, as it appears to be [20]. Thus, in fig. 1 the $P_0(Al)$ refers to the vapor pressure of monatomic Al gas over pure $Al(l)$. The calculated

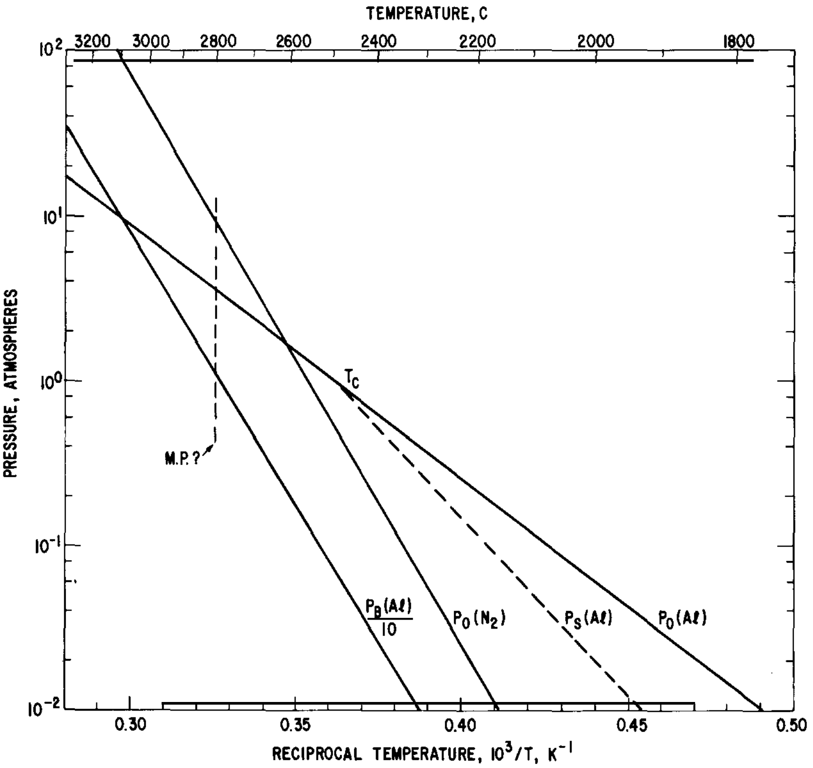

Fig. 1. Vapor or dissociation pressure versus reciprocal temperature for several systems, see text, as calculated from the JANAF tables. The critical temperature for stoichiometrically evaporating AlN is T_c. The dashed vertical line indicates the apparent melting or peritectic decomposition temperature of AlN. The several labelled curves are: $P_0(N_2)$ = pressure of N_2 over the two-phase system AlN(s) + Al(l), P_0(Al) = pressure of Al(g) over Al(l), P_s(Al) = pressure of Al(g) over AlN when the gas is stoichiometric, P_B(Al) = pressure of Al(g) over AlN when $P(N_2)$ is held at 1 atm. The curve shown is for (1/10) of P_B(Al).

boiling point of Al is 2494°C (table 1). The next step is to calculate the equilibrium constant, K, for the reaction

$$\mathrm{AlN\,(s)} \rightarrow \mathrm{Al\,(g)} + \tfrac{1}{2}\,\mathrm{N_2\,(g)}\,. \qquad (2)$$

Table 1
Important temperatures for AlN

t (°C)	Condition
3117	$P_0(N_2)$ = 100 atm [a]
2815	$P_0(N_2)$ = 10 atm [a]
2563	$P_0(N_2)$ = 1 atm [a]
2494	P_0(Al) = 1 atm [b]
2493	P_0(Al) = P_s(Al) [c]
2433	P_s(Al) = 2/3 atm

[a] Over two-phase system AlN(s) + Al(l).
[b] Boiling point of aluminum.
[c] Critical temperature when the stoichiometric gas phase is in equilibrium with the two-phase system AlN(s) + Al(l).

This can be done by combining eq. (1) with

$$\mathrm{Al}\,(l) \rightarrow \mathrm{Al\,(g)}\,. \qquad (3)$$

The K for eq. (2) is

$$K = P(\mathrm{Al})\,[P(\mathrm{N_2})]^{1/2}\,. \qquad (4)$$

If one is interested in the stoichiometric vapor over AlN(s), then $P_s(\mathrm{Al}) = 2P_s(\mathrm{N_2})$. The subscript s denotes stoichiometric. Solving $K = [P_s(\mathrm{Al})]^{3/2}\,2^{-1/2}$ for P_s(Al) versus temperature gives the corresponding curve in fig. 1. Note in fig. 1 that the P_s(Al) curve meets P_0(Al) at a temperature, t_c, of 2493°C. This means that above 2493°C solid AlN held in equilibrium with its stoichiometric vapor decomposes into Al(l) and N_2(g). This is a critical temperature for AlN because, if AlN powder is hermetically sealed into an evaluated crucible and heated up from room temperature, a liquid phase always occurs at and above

2493°C. This liquid aluminum phase invariably reacts with the crucible and destroys it. Thus, AlN(s) should never be heated above 2493°C in a sealed container. This temperature is labeled the decomposition temperature of AlN by Stull and Prophet [32]. They calculated its value as 2516°C, but 2493°C is perhaps more accurate. The closeness of this temperature to the boiling point of Al(l) is strictly coincidental.

The temperature at which $P_s(\mathrm{Al}) = 2/3$ atm is also useful because $P_s(\mathrm{N_2}) = \frac{1}{2} P_s(\mathrm{Al})$ and so $P_s(\mathrm{Al}) + P_s(\mathrm{N_2}) =$ 1 atm. This temperature is 2433°C (table 1). This is the temperature at which the pressure inside the sealed container reaches one atmosphere.

Eq. (4) shows that if the nitrogen pressure is raised above $P_0(\mathrm{N_2})$ for any fixed temperature, the $P(\mathrm{Al})$ will go down. Hence, the appearance of an Al(l) phase will be suppressed. The resulting pressure of the aluminum gas over AlN(s) when $P(\mathrm{N_2}) = 1$ atm is called the buffered pressure $P_B(\mathrm{Al})$. If $P(\mathrm{N_2}) = 100$ atm, then $P(\mathrm{Al}) =$ $[P_B(\mathrm{Al})]/10$; this is shown in fig. 1. Note that under $P(\mathrm{N_2}) = 100$ atm AlN(s) should be stable against decomposition into pure Al(l) and N_2(g) up to 3117°C. However, AlN appears to peritectically decompose or melt(?) at 2800°C [29]. Exactly how the curves in fig. 1 should be drawn above 2500°C is unclear; more experiments are needed in order to be able to tell. For example, there are no good data on the solubility of nitrogen in aluminum at these temperatures. Thus values such as t_c at 2493°C are approximations to the actual behavior.

2.2. *Surface oxidation*

Aluminum nitride is unstable in air at room temperature, as is aluminum metal. Both react with moisture and/or oxygen in the air to form a surface layer of aluminum oxide. This layer is protective and retards further oxidation. On aluminum metal, this surface oxide layer grows to a thickness of about 30 Å in one day [33–35].

For AlN measurements made in this laboratory using neutron activation [36, 37] on high surface-area powder, supplemented by optical ellipsometry [38] on single crystals, indicate that on AlN an oxide thickness of 50 to 100 Å forms in one day at room temperature. By way of contrast, the surface oxide on AlP crystals is unprotective [39], and the crystals readily decompose in moist air to $Al_2O_3 \cdot 3H_2O$ and PH_3.

3. Production of AlN powder

3.1. *Aluminum metal plus gas*

The compound AlN was first made [40] in 1862 from liquid Al and N_2 gas. The major difficulty in such a direct reaction method is that the surface film of AlN on the Al is very adherent and impedes further reaction. Some experiments run in this laboratory and elsewhere [41] have shown that in 1 atm pressure of N_2 the protective surface film on liquid Al begins to break down only at temperatures above 1500°C.

In another technique AlN powder can be formed from Al electrodes in a direct current arc. This technique was first reported by Ahrons [42], and others subsequently [20, 43]. The method produces only small amounts of AlN per day, and the powder usually has several per cent of excess aluminum because even here the AlN skin is protective.

Some success at making AlN has been achieved by exposing either Zn–Al [44] or Hg–Al [45] alloys to N_2 or NH_3 at high temperatures.

3.2. *Reaction of AlF_3 with NH_3*

The most satisfactory method that we have found so far for making pure AlN is to react AlF_3 powder with NH_3 gas at high temperatures. A variation of this has been described by Rabenau [46]. Funk and Boehland [47], and Hejduk [48]. The reaction at high temperatures near 1000°C is:

$$AlF_3\ (s) + NH_3\ (g) \rightarrow AlN\ (s) + 3\ HF\ (g)\,. \qquad (5)$$

In order to promote the formation of AlN in eq. (5) it is best to keep the NH_3 partial pressure as high as possible, i.e. near 1 atm. This is accomplished by using a Pt–10%Rh furnace tube in fig. 2 because the NH_3 dissociation, which occurs only on the furnace walls or on the AlF_3 powder, is much reduced from what it would be with molybdenum or other walls by the adsorbed H_2 layer on Pt–10%Rh.

In order to make eq. (5) go toward completion, the HF gas must be continually removed. At one atmosphere pressure of NH_3 a minimum of about 25 molecules of NH_3 are needed for each molecule of AlN produced. Our measurements show that when this ratio is raised to 400 the resulting AlN powder contains about 0.6 wt% of fluorine (as AlF_3) as a re-

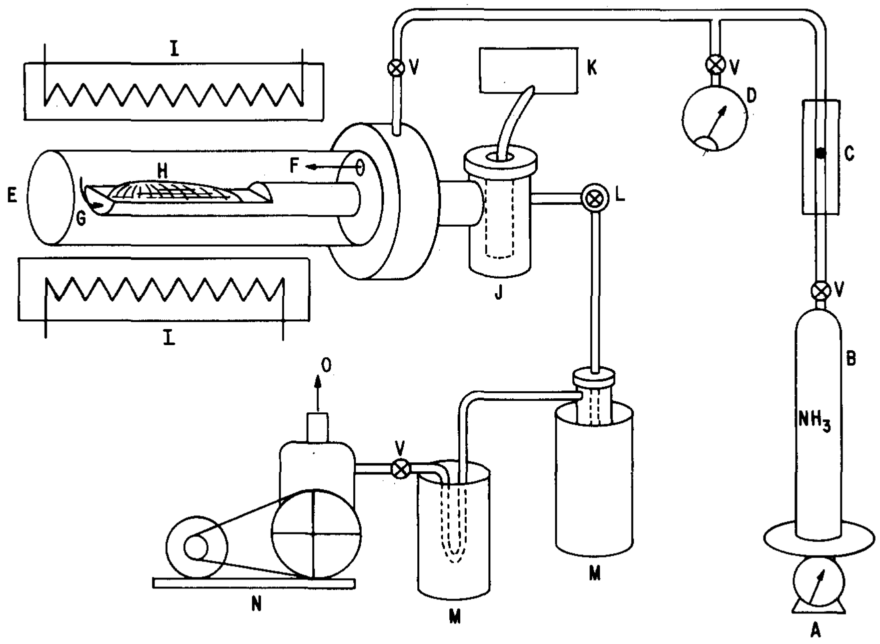

Fig. 2. Platinum–10% rhodium tube furnace arranged for converting AlF_3 powder to AlN powder. The piping is monel or stainles steel. (A) scales, (B) ammonia tank, (C) flow meter, (D) pressure gauge, (E) 90% Pt–10/Rh chamber, (F) NH_3 inlet, (G) gas outlet, (H) AlF_3 powder, (I) 60%Pt–40%Rh resistance furnace (J) −37° cold trap, (K) cold probe refrigerator, (L) pressure reducing throttle valve, (M) −78° dry ice bath, (N) vacuum pump, (O) vent, (V) valve.

sidual. The residual AlF_3 can be removed from the AlN powder by mixing the resultant powder and further treating it with NH_3, or by heating the powder above 1260°C to evaporate the AlF_3. The vapor pressure [49–54] of solid AlF_3 reaches 1 atm at 1260°C. The AlF_3 + AlN mixture, must, however, be removed from the plantinum tube furnace for this operation. If AlN is heated in contact with Pt above the temperature of the Al–Pt eutectic at 1260°C [55] the AlN is decomposed.

The sublimation of the residual AlF_3 from the AlN can be carried out at 1400°C to 1450°C in a tungsten or molybdenum tube furnace. In this way the residual concentration of fluorine has been reduced to 0.04 wt%. The presence of AlF_3 in the AlN is undesirable, because it interferes with the neutron activation analysis [36, 37] for oxygen in the AlN. It may also cause excessive pressure build-up in the sealed crucibles when the AlN is used for crystal growing.

The NH_3 gas used in eq. (5) needs to have a very small H_2O and O_2 content. The NH_3 is purchased as liquid NH_3 with <10 ppm of H_2O or O_2. These residual gases are removed by introducing about 1 gram of metallic Na per liter of liquid NH_3 into the stainless steel storage vessels. This technique of purifying NH_3 has been used for many years [56–58].

3.3. Aluminum nitride fluoride

So far, it has been assumed that AlN and AlF_3 do not react to form the compound aluminum fluoride nitride. Recently, such compounds have been found [59–63] for Mg, Ca, Sr, Ba, La and U. An experiment was performed in which high purity AlN powder and AlF_3 powder were mixed in such a proportion that they might make $Al_4N_3F_3$ in analogy with Al_2O_3. The powders were heated together for 4 h at 1250°C in an evacuated and sealed tungsten crucible. Both visual and X-ray examination of the product showed only AlN and AlF_3 at the end of the run. Hence, no aluminum fluoride nitride compounds were made or exist in the temperature range of interest. Thus the conversion of AlF_3 with NH_3 should proceed directly to AlN with no intermediate compounds.

3.4. Chemistry of AlF_3

The purity of the AlF_3 used in making the AlN powder is of prime importance. It is relatively easy to keep the level of metallic impurities in AlF_3 at acceptable levels of 10 ppm or less by starting with pure Al metal. The really difficult problem is to keep the oxygen content of the AlF_3 low. Commercial AlF_3 powder (anhydrous AlF_3) is usually made by thermally decomposing $AlF_3 \cdot 3H_2O$ [64–66]. This decomposition by heating in air to about 200°C proceeds easily to $AlF_3 \cdot \frac{1}{2} H_2O$. At this point, the crystal lattice has collapsed sufficiently [67] so that the last water molecule is trapped in what would be a normally vacant site in the pure AlF_3 crystal. Upon prolonged heating the resultant AlF_3 normally contains about 3 wt% oxygen as Al_2O_3. It has been suggested [68, 69] that AlF_3 contaminated with Al_2O_3 can be purified by sublimation. Such sublimation experiments have been carried out in this laboratory, but the resultant AlF_3 always had a few tenths of a weight per cent of oxygen in it. Presumably the oxygen is carried over as oxyfluoride vapor molecules, AlOF [70–72].

Higher purity AlF_3 can be made from ammonium cryolite $(NH_4)_3AlF_6$ by thermal decomposition. The $(NH_4)_3AlF_6$ is made [73] from Al metal, aqueous HF, and NH_4OH. The decomposition [74–76] proceeds by liberation of NH_4F via NH_4AlF_4 to γ-AlF_3 and finally to α-AlF_3. Such AlF_3 made here customarily contained 0.2 wt% oxygen. This oxygen analysis was performed [77] at Oak Ridge National Laboratory by dissolving the AlF_3 powder in molten $KBrF_4$ and collecting the liberated oxygen.

The residual oxygen in either sublimed AlF_3 or AlF_3 made from $(NH_4)_3AlF_6$ can be removed by heating the AlF_3 powder in a stream of anhydrous HF gas [78] at 1000°C in the Pt–Rh furnace (fig. 2). When HF gas [79] containing 0.04 wt% H_2O was used at 1000°C for 24 h, the resultant AlF_3 contained 150 to 300 ppm of oxygen. Even lower oxygen contents are desirable.

The best process so far found in this laboratory for making high purity AlF_3 is to react Al metal directly with HF gas. The first part of the reaction is carried out at 600°C; below the melting point of Al at 660°C. The Al metal [81] is used in the form of 0.025 cm thick sheet. The conversion of Al to AlF_3 is linear in time [82]; the AlF_3 layer is not protective. The conversion rate at 600°C and an HF pressure of 1 atm is about 0.003 cm/h. After 24 h about 95% of the Al metal has been converted to AlF_3 and the result is a light grey powder. If the temperature is now raised to 1000°C the reaction goes to completion and the powder has 50 ppm of oxygen. No metallic impurities >10 ppm were detected. This reaction is carried out in the Pt–Rh furnace where the Al strip is held in a glassy carbon [83] boat.

3.5. Hygroscopic nature of AlF_3

Once AlF_3 powder has been prepared with a very low oxygen content, it must be kept away from water vapor in the atmosphere. It it is not, it will slowly convert to $AlF_3 \cdot \frac{1}{2}H_2O$. The equilibrium H_2O pressure [65] over $AlF_3 \cdot \frac{1}{2}H_2O$ is 0.8 Torr at 27°C. Thus, the powder has to be handled in a dry box and stored under a dry atmosphere.

3.6. Hygroscopic nature of AlN

If AlF_3 with only 50 ppm by weight of oxygen is used in eq. (5), and if all of this oxygen is retained by the AlN formed, the oxygen concentration in the AlN powder will be 100 ppm. By using neutron activation the lowest oxygen concentration found in the AlN powder made by this method was much higher, about 3000 ppm. The source of this large amount of oxygen appears to be the rapid reaction of the AlN with atmospheric moisture when the powder is removed from the furnace, see fig. 2. Consider a 100 Å thick layer of Al_2O_3 on particles of AlN powder 2 μm in diameter. If all of the particles were coated in this manner, the average oxygen content of the AlN would be 2000 ppm by weight. Since the oxidation of AlN is strongly exothermic, there is no way of reducing the H_2O content of any dry box in which the AlN powder is handled to a level where the oxidation never occurs.

4. Impurities in AlN

An understanding of which elements might act as impurities in AlN is important in growing crystals of high purity. Atoms with tetrahedral radii close to those of Al and N would be those most apt to substitute for Al or N. Values for such radii can be taken from

Pauling [84], or Phillips [85]. Consider only those impurities which would be isoelectronic or act as single donors or acceptors. A difference in radii of 0 to 10% indicates a high solubility, a 10 to 20% difference indicates a moderate to low solubility, and greater than 20% indicates a very low solubility. These criteria indicate that C and O should have a high solubility in the Al sublattice; and Be, Cd, In, Hg, Tl, and Pb should have a moderate to low solubility in the Al sublattice. In considering the common amphoteric impurities, note that C will not readily replace Al, nor will Si, Ge or Sn readily replace N.

A second criterion that should be applied is the stability of the impurity-to-lattice bonds at the temperatures at which the crystals are grown or annealed. This means that for C or O to be substitutional impurities in AlN crystals, the compounds Al_4C_3 or Al_2O_3 should be stable to a temperature of at least 1500°C. Both are stable to this temperature. The compound Al_2O_3 melts congruently [86] at 2051°C; the compound Al_4C_3 decomposes peritectically at 2135°C [87]. Thus both C and O are expected to act as highly soluble impurities in AlN by substituting for N.

Of the possible nitrogen compounds only Mg_3N_2, Si_3N_4 and Be_3N_2 exist [88–90] above 1000°C at a pressure of 1 atm of N_2 gas; for temperatures above 1500°C only Si_3N_4 and Be_3N_2 exist. Thus Si and Be should be considered as possible substituents for Al.

If we consider the first transition metal series, their tetrahedral radii [91], and the stability of their nitrides [88, 89], then Ti, V and Mn might well substitute for Al in AlN.

What data are available in the literature to test these hypotheses about impurities? Oxygen is a well known impurity in AlN. It can be present in high concentrations [92] up to $1.5 \times 10^{22}/cm^3$ and its incorporation reduces [92] the lattice parameters of AlN. The solubility of Al_4C_3 in AlN has not been systematically studied, however, many different aluminum carbonitrides exist [93, 94]. The solubility of carbon or carbon–oxygen complexes in AlN is sufficient to produce p-type crystals of low electrical resistivity [17], i.e. about 10^3 ohm cm at room temperature. Both C and O together in the form of Al_2CO are soluble in AlN up to rather high concentrations. The crystal structure [95] of Al_2CO is the same as that of AlN. Solubilities up to 14 mole% Al_2CO in Al_2N_2 have been measured [96]. In all probability there is a continuous range of solid solutions from AlN to nearly pure Al_2CO. In fact Al_2CO does not appear to be a stable phase in itself, but requires a small amount of AlN to stabilize it [87]. Since one expects C to act as an acceptor when replacing N, and O to act as a donor, then Al_2CO additions should be electrically inactive in AlN. A net acceptor concentration is probably produced only when the C content exceeds the oxygen content.

As for isoelectric replacements for N, Addamiano [97] found that AlN will not form mixed crystals with AlP. This is in agreement with the radius of P being much larger than that of N.

For substitutions in the Al sublattice the work by Tiede et al. [98] indicated that up to 5 wt% Si can be put into AlN. More recent work by Kamyshov et al. [99] indicates a maximum solubility of 0.12 wt% Si or $8.8 \times 10^{19}/cm^3$ of Si atoms. The addition of Si is reported to make AlN n-type [100, 101], which is the behavior that would be expected if Si replaces Al. There are no reports in the literature on Be doping of AlN. However, Be doping has been used to make p-type cubic BN [102], BP [103], GaP [104, 105], SiC [106], and Be is soluble in GaN [107]. Hence Be may well act as a p-type dopant in AlN. The behavior of Mg in AlN has been studied once [108], it gives p-type AlN. Additions [104, 109] of Mg to GaP make it p-type, Mg in GaN makes [107] it high resistivity, while Mg seems [102] to be too large to enter the lattice of cubic BN.

GaN apparently [110] forms mixed crystals with AlN over the whole composition range, and the Ga acts as an isoelectronic substituent for Al. The solubility at high temperatures may be very low because of the instability [90] of GaN. Mixed crystals of AlN and SiC have been made [111–113], presumably over the whole range of composition [113]. Note that the interatomic distances in AlN, SiC, and GaN are equal to within 3%. Since Si acts as a donor and carbon as an acceptor in AlN, then SiC dissolved in AlN should be electrically neutral to a first approximation.

A few of the impurities that probably have low solubility in AlN have been studied. Sulfur has been found to affect [113, 114] the electrical resistivity of AlN. If S substitutes for N, it should be an n-type dopant, in contrast to the reported behavior [113]. This report in the patent literature may be in error. Sulfur impurities in cubic BN yield [102] n-type crystals. Several articles [108, 114, 115] deal with Zn, Cd, Hg or Se additions to AlN.

Both n-type and p-type AlN have been produced by several different techniques [94, 100, 113, 115]. Thus AlN behaves similarly to cubic BN, which has been made [102] both n-type and p-type. By contrast GaN has, to date, only been made n-type [107]. These results on AlN are in agreement with the speculation of Dismukes et al. [116] that AlN of both conductivity types can be made. They disagree with Mandel et al. [117], who state that only p-type AlN is possible.

Other elemental impurities have been put into AlN in order to alter the luminescence properties rather than the electrical properties. Mn has been used and studied by numerous authors [118–124]. A few people [120, 123, 125] have studied the luminescence of rare-earth impurities in AlN. The solubility of Mn in AlN should be moderately large. The Mn–N average tetrahedral distance in $MnSiN_2$ crystals is [126] 2.04 Å, while in AlN the Al–N distance is 1.89 Å. The difference in distances is only 8%. Using a N radius of 0.70 Å, the Mn radius is 13% larger than that of Al. The rare-earth ions are considerably larger than Al (about 50%), hence their solubilities should be much lower than that of Mn.

Thus, one should expect Be, C, O, Mg and Si to have high solubilities in AlN and, potentially, to act as donors or acceptors. Other impurities such as S, Mn, or the rare earths may have important properties, but will probably possess lower maximum solubilities.

Some estimate of the impurity activation energies is useful. The effective mass binding energy is [127]

$$E_B = 13.6(m^*/m_0K^2)\ \text{eV}. \quad (6)$$

The static dielectric constant, K, of AlN is [15] $K = 9.1$. If the effective mass is, as a guess, $1.0m_0$, then

$$E_B = 0.16\ \text{eV}. \quad (7)$$

The smallest activation energy for electrical conduction that has been observed [128, 129] is 0.5 to 0.6 eV in AlN. The ionization energies of donors and acceptors in GaN are [130] 0.04 and 0.2 ev respectively. These energies in cubic BN range [102] from 0.05 to 0.2 eV. Thus eq. (14) should give an approximate value for impurities in AlN. The one exception might be oxygen. Oxygen has been found [131] to be a very deep donor in GaAs and GaP. In GaP the ionization energy is 0.9 eV. In AlN it is probably even larger. Since oxygen is a common impurity in almost all crystals of AlN, it may dominate or severely modify the electrical behavior.

5. Removal of oxygen from AlN

Aluminum nitride powder covered with a surface oxide can conceivably be purified by heating in a gas stream of high purity NH_3. Thus,

$$2\,NH_3\,(g) + Al_2O_3\,(s) \rightarrow 2\,AlN\,(s) + 3\,H_2O\,(g)\,. \quad (8)$$

If a large quantity of NH_3 is used, a small quantity of H_2O will be removed at 1000°C. The above reaction is strongly endothermic, hence, a large amount of pure NH_3 is needed to remove a small amount of Al_2O_3.

A better method of removing the Al_2O_3 is by sublimation at even higher temperatures. This technique has been used by others [20, 43]. The oxygen is removed by the formation of volatile aluminum suboxide approximately as:

$$Al_2O_3\,(s) + 4\,AlN\,(s) \rightarrow 3\,Al_2O\,(g) + 2\,N_2\,(g)\,. \quad (9)$$

The formation of Al_2O as a gaseous species over Al_2O_3 + Al at high temperatures has been seen in a mass spectrometer by various authors [132–134]. Its dissociation energy [134] is 10.9 eV. The dissociation energies for a number of other important diatomic molecules have been listed by Gaydon [135]. For triatomic and tetra-atomic molecules, other sources [136–142] have been used.

We ran experiments with impure AlN powders containing 3 wt% Al_2O_3 and have verified that the oxygen can be preferentially distilled leaving purer AlN behind. If the temperature is sufficiently high, the AlN particles also exhibit a substantial increase is size via localized vapor transport. Hence, their surface area is also greatly reduced, as well as the possible oxygen pickup by surface reoxidation when later exposed to room air. In the experiments, the powder is sealed inside a tungsten crucible which is filled to about 50% of capacity and is then placed in a radio-frequency induction furnace (fig. 3). The lower end of the crucible is heated to 2200°C while the top end is only 2050°C. After 4 to 8 h running time, the cooler end of the crucible is coated on the inside with a densely packed layer of colorless, transparent aluminum oxynitride whiskers and needles. These do not have the AlN crystal structure, but possess a more complex hexagonal structure. Analysis indicates about 10 wt% oxygen. A few crystals of amber-colored AlN are also occasionally found in the cooler end. The oxygen analysis of the AlN

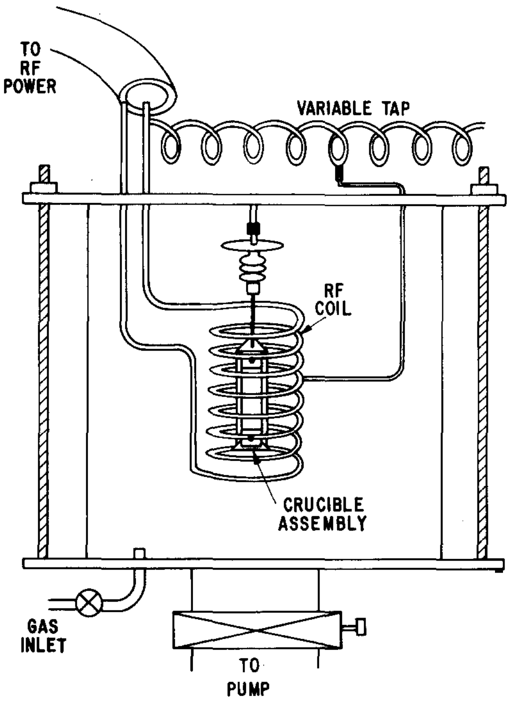

Fig. 3. High-temperature radio-frequency induction furnace for heating sealed crucibles to temperature of 2500°C in an inert atmosphere or vacuum. The variable tap permits one to vary the longitudinal temperature profile of the crucible.

from the hotter end shows 2000 ppm by weight. The oxygen content has decreased by a factor of 7. If this AlN is reheated in a second tungsten crucible at 2300°C for 6 h, the oxygen content can be reduced to about 600 ppm. A third run has given a few grams of AlN with as little as 350 ppm of oxygen. This AlN is lower in oxygen than any other samples mentioned [43] in the literature by a factor of 6.

6. Sublimation growth of single crystal AlN

6.1. *AlN used as the source*

The most satisfactory methods of growing high purity AlN single crystals appear to be those where AlN itself is used as the starting material. Since high temperatures (i.e., 1500°C or above) are required, contamination from crucibles is always a problem. By using an arc image furnace, Evans and Davies [143] were able to grow whiskers 1.6 mm long by 0.02 mm in diameter. Using the focused arc, they locally heated AlN ceramic under $P(N_2)$ of 1 atm. In their method the temperature gradients were very large; therefore, it would be difficult to grow large crystals. However, no crucible is involved.

Another possibility is to use some crucible material that melts above 2500°C. For the elements this means crucibles of Mo, Os, Ta, Re, W, or C. Molybdenum is ruled out because of its low-melting eutectic [144] with Al at 1760°C; Os is too expensive and toxic; and Ta reacts too readily with N to form Ta_2N and TaN. This leaves Re, W, C, or perhaps TaN. Tungsten crucibles were first used by Fichter and Oesterheld [145]. They also showed that carbon crucibles contaminate the AlN with carbon and aluminum carbide. Sata and Urano [146] showed that tungsten does not react with AlN up to 2100°C; while Class [29] always found a reaction above 2300°C, even at high N_2 pressures up to 100 atm.

In experiments in this laboratory high purity AlN powder has been heated in sealed W crucibles up to 2275°C with no visible attack. The Al content of the W at this temperature rises to 400 ppm by weight, while the W content of the AlN is about 50 ppm. At 2300 ± 25°C there is a rapid attack by Al vapor at the grain boundaries of the tungsten crucible at $P(N_2) =$ 1 atm. This takes the form of an intergranular liquid phase in the W and leads to small pin-holes (up to 5 μm in diameter) through the walls of the W crucible, particularly at the triple-points where three tungsten grains meet. The integrity of the crucible is not immediately ruined by this grain-boundary attack. On the average, the Al content of the W rises to about 1500 ppm at 2350°C. For short times of about 30 min, sealed W crucibles containing AlN have been heated to 2450°C in an external N_2 pressure of 1 atm without gross failure. From table 1 it can be seen that the total internal pressure is slightly greater than one atmosphere at this temperature. With only an external pressure of one atmosphere of N_2 the crucibles failed before we reached t_c = 2493°C.

Rhenium has been used [29] in contact with AlN up to 2700°C with $P(N_2)$ = 100 atm. Above this temperature a liquid phase formed. In our experiments a liquid phase occurred at 2380°C with $P(N_2)$ = 1 atm. At 2370°C the Al content of the Re due to the absorption of Al(g) from the AlN was measured as 1000 ppm by weight. This is comparable to that found for W. The

Re content of the AlN was 60 ppm by weight, not much higher than the W content when W crucibles were used. So Re is not significantly better than W at $P(N_2) = 1$ atm.

Carbon (i.e., graphite) crucibles or furnace tubes containing AlN have been used by many [9, 25, 94, 108, 129, 147–150] people for growing AlN crystals from AlN powder. Class [29] has shown that at $P(N_2) = 100$ atm no liquid phase occurs until 2800°C is reached. The main disadvantage of carbon is carbon impurity in the crystals.

6.2. *Sublimation using Al or Al_2O_3 sources*

Others [9, 151–154] have used Al as the starting charge in graphite crucibles or tube furnaces with a flowing N_2 atmosphere. Another variant uses [155–157] Al_2O_3 in graphite furnaces with flowing N_2 gas. This latter method depends on the Serpek process [21] reaction. This process has been used commercially by the Pechiney Compagnie for producing AlN, and some of the largest crystals of AlN ever produced have been accidentally grown in their furnaces [158–160]. Crystals up to 1.5 cm long and 0.3 cm in diameter have been found [92, 161]. The furnaces are a meter or more in size, and the masses of the AlN charge are greater than tens of kilograms. Yet another crystal growing technique [162] uses AlN placed in an Al_2O_3 tube furnace with flowing N_2 gas.

6.3. *Critique*

The AlN plus W or Re systems, as used in this laboratory, lead to very little contamination of the AlN with metal impurities. The arc-image furnace method [143] may be even cleaner. In all of the other methods, either carbon or oxygen or both may end up in the AlN crystals. In the AlN + C system at high temperatures vapor molecules of AlCN, AlC_2, Al_2C_2, C_2 and CN may all exist [135–142] to provide carbon atoms in the vapor from which the crystals are growing. The presence of AlCN in the vapor turns out to have significant importance in commercial [159] AlN furnaces, and is present in large quantities. When the system is AlN + C + Al_2O_3, many more vapor species are present, and both oxygen and carbon can be incorporated into the growing crystals in varying ratios. Such crystals often exhibit bands of yellow, blue, brown, or colorless regions in rapid succession, presumably caused by rapid changes in the gas atmosphere. By contrast, the crystals grown in W or Re crucibles are generally of uniform amber color. Thus both oxygen and carbon should be scrupulously avoided in the furnace construction or in the source material if high purity AlN crystals are desired.

6.4. *Sublimation with a carrier gas*

In addition to sublimation in a closed tube in a temperature gradient, it is possible to aid the transport by use of a carrier gas. One such scheme is shown in fig. 4. A thin wall tungsten tube 2.5 cm in diameter by 30 cm long is held in a fused quartz apparatus and is heated by a radio frequency induction heater. The hot zone with the AlN charge is held at 2000 to 2250°C, the gas stream of NH_3, $N_2 + H_2$, or pure N_2 is passed

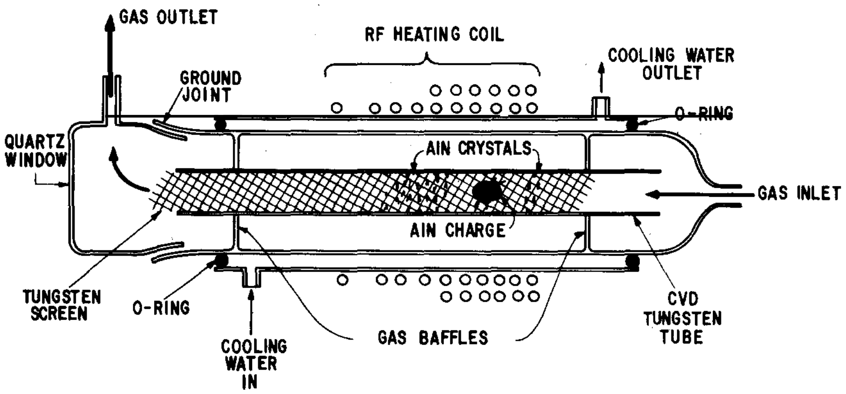

Fig. 4. Tungsten tube furnace used for growing AlN crystals in a flowing gas stream. The tungsten wire screen provides a large nucleation surface for crystal growth.

over the charge, and the crystal grow on the inner walls of the tube at 1700 to 2000°C. Crystals up to 1 mm wide and 1 cm long have been grown in this furnace in a time of 6 h.

6.5. *Other sublimation experiments*

Extensive experiments on sublimation growth of AlN have been carried out by Campbell and Chang [108] and by Knippenberg and Verspui [113]. In the Campbell and Chang experiments rather impure AlN powder containing both carbon and nitrogen impurities was used, temperatures of 1950 to 2200°C were employed, and graphite crucibles were used. Crucibles of Ta, Mo, SiC, and Al_2O_3 were also tried, but were mostly unsuccessful. Plate-like crystals up to 1 mm across were produced in the graphite crucibles. No impurity analyses were made on these crystals. but an extensive report of crystal morphology was made [108].

The experiments of Knippenberg and Verspui were carried out between 1800 and 2300°C in graphite crucibles. Sometimes [46] tantalum nitride liners were used inside the graphite crucibles. Sometimes crystals were grown on AlN and sometimes on SiC platelets as substrates. Crystals up to a few millimeters in size were produced. Some studies on these crystals have been reported [163].

7. Other growth techniques

7.1. *Vapor cracking*

A variety of techniques other than sublimation are of possible use for AlN. A common method used for making thin films of AlN is to use the aluminum halide–ammonia complexes such as $AlX_3 \cdot NH_3$. They are decomposed at temperatures of 800 to 1500°C on heated substrates to yield AlN. This method was used by Tiede et al. [98], and by numerous others [2,164–171] since. The trimethyl aluminum version has been tried by several people [172, 173]. These methods produce thin films of AlN at a slow rate of 1 to 30 μm/h. The films usually contain excess chlorine [171] as an impurity as well as oxygen, and may contain carbon if $Al(CH_3)_3$ is used [172, 173]. One of the serious problems encountered when this method was tried in this laboratory was the unavoidable pickup of oxygen. Furthermore, the hot $AlCl_3$ vapor reacts [174] with the SiO_2 walls of the apparatus to give both oxygen and silicon contamination. In several experiments the oxygen content of the pyrolytic AlN films was 2.2 wt%. The method was not pursued further.

7.2. *Plasma torch, rf sputtering, etc.*

Several techniques have been employed to break up the N_2 molecules before combining them with Al. Small crystals of AlN have been grown in a N_2–Cl_2 low-pressure plasma torch by Veprek et al. [175]. No data on purity or perfection were given. The crystals were quite small in size. The literature on similar techniques for thin films is fairly extensive [176–184]; none of these seem applicable to the growth of large crystals of AlN. In all of them the mass transport per unit time is quite small.

7.3. *Flux growth*

Because of the difficulties associated with the growth of AlN by sublimation at high temperatures, it would be attractive to reduce the temperature by using precipitation of AlN from a suitable solvent or flux at lower temperatures. Liquid iron is a solvent [185–187]. Whiskers of AlN have been grown [156,188] from drops of liquid Fe by the vapor–liquid–solid or VLS mechanism.

Growth of AlN from liquid iron has been tried in this laboratory. High purity iron with the addition of a few percent of high purity aluminum was melted in a hot-pressed AlN crucible and held at a temperature of 1600 to 1700°C for 6 h. One experiment was run in NH_3 gas at 1 atm pressure, and a second was run in N_2 gas at 82 atm. In both cases, the amount of AlN transported was discouragingly small. Some water white crystals 1 mm by 0.1 mm were grown. The nitrogen solubility is low [186] and increases only as $\sqrt{P(N_2)}$. In order to increase the nitrogen solubility, an alloy of 40% Fe plus 60% Mn was held at 1400°C in a small temperature gradient for 76 h in a $P(N_2)$ of 5×10^4 atm in a high-pressure press [189]. A number of 0.1 mm size crystals of AlN were grown. They were water white in color but had substantial amounts of Mn in them, which produces a characteristic orange-red luminescence.

Campbell and Chang [108] report an attempt to grow AlN from molten Na_3AlF_6, cryolite. The solvents Li_3N, Mg_3N_2, and Ca_3N_2 have been used [190,191] for growing BN crystals at high pressures. Molten Ca_3N_2 has been used by Dugger [192] for growing AlN crystals in sealed crucibles at or below 1600°C.

7.4. Chemically aided vapor transport

In order to reduce the temperature needed for AlN growth below 2000°C, it may be possible to use a variety of chemical transport reactions [193]. Some experiments using Cl at 1200°C in sealed tubes have been reported by Chu et al. [194]. The transport rates were very small. The most promising transport system, based on work done in this laboratory appears to be one using AlF as the carrier gas. The reaction is

$$AlF_3 + 2\,AlN \rightleftarrows 3\,AlF + N_2\,. \qquad (10)$$

The reaction

$$AlF_3 + 2\,Al \rightleftarrows 3\,AlF \qquad (11)$$

has been studied by Ko et al. [52]. By combining their results with the thermodynamic data [32] for AlN, one can calculate the quilibrium constant for eq. (10). The equilibrium constant is unity at 1760°C. This means that AlF_3 gas can be used to transport AlN from a source at a higher temperature to a sink at lower temperature. Crystals of AlN can grow at a sink temperature of 1500 to 1700°C. One such setup in this laboratory involved an 8 cm long sealed tungsten tube about 1 cm in diameter placed in a two-zone furnace. The hotter zone, at one end, is the location of the AlN powder source at about 1800°C. The colder zone, the other end, holds AlF_3 powder at about 1200°C with a vapor pressure of about 0.36 atm. The AlF_3 vapor reacts with the solid AlN at 1800°C to give AlF and N_2. The reaction products drift down the temperature gradient to about 1600°C where they reform to give AlN and AlF_3. A substantial amount of AlN was transported in 6 h time. An X-ray analysis showed the correct lattice parameters. The presence of large amounts of F in the gas phase did not alter the crystal structure or the lattice parameters. All of the crystals formed were very small, so that control of nucleation may be a problem with this method.

8. Characterization of AlN crystals

Several different physical measurements have been made on the single crystals and on the polycrystalline aggregates grown in this laboratory. Pure AlN has extrapolated [92] lattice parameters of $a_0 = 3.1127 \pm 0.0003$, $c_0 = 4.9816 \pm 0.0005$ Å at 25°C. The X-ray density of pure AlN is [92] 3.255 g/cm^3 at room temperature. We have measured flotation density at room temperature of AlN single crystals as 3.260 ± 0.001 g/cm^3 for sample R169 (see ref. [92]) grown by Pechiney [158]. The calculated X-ray density for this particular crystal was 3.257 ± 0.001 g/cm^3. The flotation density was 3.261 ± 0.001 g/cm^3 for the samples in fig. 5. Samples grown by sublimation in a flowing $N_2 + H_2$ gas stream had a density of 3.257 ± 0.001 g/cm^3. The density difference of 0.004 g/cm^3 between these two samples is a real effect, and is probably related to a difference in purity or stoichiometry. These densities were determined by making a liquid mixture of CH_2I_2 (diiodomethane) and C_6H_6 (benzene) in which the crystals would just barely float or sink. The liquid density was then measured by using a weighing bottle.

Fig. 5. Some crystals from furnace in fig. 3. The scale divisions are 1 mm apart.

The indentation microhardness of some of the AlN single crystals from fig. 5 has been measured as 1200 to 1550 kg/mm^2 in room air at room temperature. These values are in general agreement with values in the literature [9–11].

The thermal expansion of AlN has been measured [7], and is comparable in magnitude and temperature dependence to other crystals with a diamond-like crystal structure.

Crystals up to 3 mm long and 1 mm have been grown in this laboratory by sublimation of AlN powder in sealed tungsten crucibles. Three crystals grown this way are shown in fig. 5. They are clear, transparent, and amber yellow in color. Crystals grown in rhenium crucibles are the same color. The yellow coloration is probably caused by a nitrogen deficiency in the lattice. This deficiency may be caused either by nitrogen vacancies or aluminum interstitials. The excess aluminum theory has been proposed previously [17,129]. A typical optical absorption coefficient versus photon wavenumber curve for AlN is shown in fig. 6. The lattice phonon bands [15,18,19] produce the absorption for $\bar{\nu}$ values below $\bar{\nu} = 2000$ cm^{-1}.

The two phonon absorption region has been studied by Pastrnak and Hejda [19] and by Collins et al. [15]. The absorption peak at $\bar{\nu} = 1990$ cm^{-1} in fig. 6 is caused by the generation of three transverse optic phonons. Between $2500 \leqslant \bar{\nu} \leqslant 43{,}000$ cm^{-1} pure, stoichiometric AlN should show no optical absorption, i.e. the absorption coefficient, α, should be <1 cm^{-1}. The steep rise for $\bar{\nu} > 43{,}000$ cm^{-1} is based on the work of Yim et al. [2] on thin films. The residual absorption for $5000 \leqslant \bar{\nu} \leqslant 43{,}000$ cm^{-1} where $1 \leqslant \alpha \leqslant 10^3$ cm^{-1} is shown in more detail in fig. 7. Here the results on a number of samples made in this laboratory are shown. The dominant defects in these samples are oxygen impurities and deviations from stoichiometry. Fig. 7 shows, as in sample PF, a broad, featureless absorption rising from $\alpha = 1$ cm^{-1} at $\bar{\nu} = 6000$ cm^{-1} to $\alpha \geqslant 10^3$ cm^{-1} for $\bar{\nu} \geqslant 40{,}000$ cm^{-1}. In addition a peak occurs in other samples at $\bar{\nu} = 23{,}070$ cm^{-1} superimposed on top of the featureless rise.

Lagrenaudie [128] has seen an absorption band in AlN at $\bar{\nu} = 25{,}000$ cm^{-1}, but made no assignment as to its cause. Pastrnak and Roskovcova [6] found absorption bands at $\bar{\nu} = 36{,}540$ cm^{-1} and 38,720 cm^{-1}

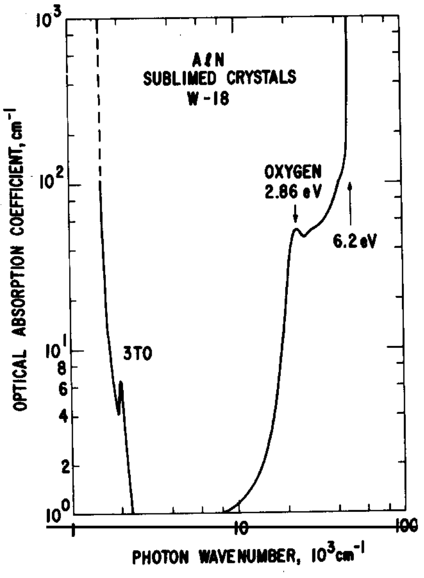

Fig. 6. Optical absorption coefficient versus photon wavenumber for AlN. The 3TO peak in the infrared is clearly visible. The peak at $\bar{\nu} = 23{,}070$ cm^{-1} (2.86 eV) is probably caused by oxygen impurities. The fundamental absorption edge occurs at $\bar{\nu} = 50{,}000$ cm^{-1} (6.2 eV).

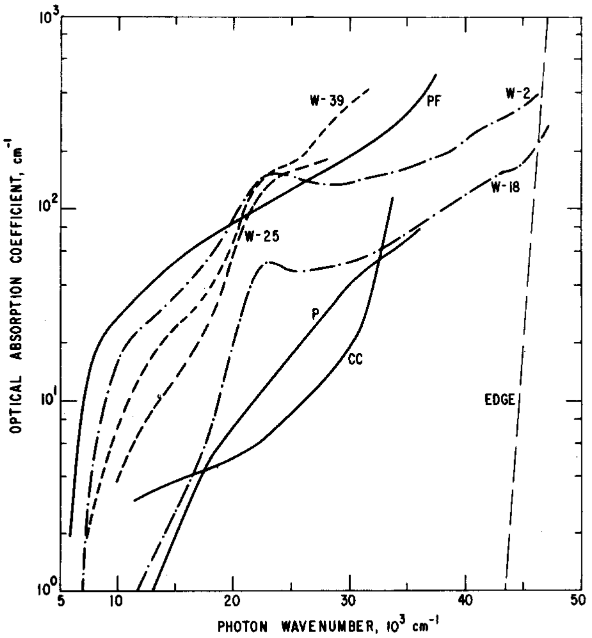

Fig. 7. Optical absorption coefficient versus photon wavenumber for AlN. See table 2 for a description of the samples. The absorption-edge line is an extrapolation of data from ref. [2].

Table 2
Optical absorption samples

Sample	Growth temperature (°C)	Oxygen content (wt%)	Oxygen concentration (atoms/cm^3)
W-2	2090	>0.5	$>6 \times 10^{20}$
W-18	2130	0.16	2.0×10^{20}
W-25	2300	0.054	0.66×10^{20}
W-39	2330	$\sim$0.08	$\sim 1 \times 10^{20}$
PF	1000	?	?
P(R169)	>1700	0.2 ± 0.1	$(3 \pm 2) \times 10^{20}$
CC	$\sim$2000	?	?

which they attributed to oxygen. Kawabe et al. [17] and Cox et al. [129] found a band at $\bar{\nu} = 22{,}600$ cm^{-1} which they attributed to excess aluminum. Yim et al. [2] found only a broad, featureless rise in $\bar{\nu}$ over the range $29{,}000 \leqslant \bar{\nu} \leqslant 43{,}000$ cm^{-1}. From these previous results it is rather difficult to ascertain the cause of the extrinsic absorption in fig. 7. Let us see what can be concluded from an analysis of the samples studied in fig. 7 as listed in table 2. The samples W-2, W-18, W-25 were polycrystalline deposits grown in tungsten crucibles. The tungsten substrate on which they grew was etched away, and the deposits were polished to obtain successively thinner pieces for the optical measurements. Sample W-39 was prepared similarly, but it was grown in a Re-lined W crucible. Sample PF was a 0.007 cm thick polycrystalline deposit grown on Pt at 1000°C from a mixture of AlF_3 gas and NH_3 gas. It was produced accidentally during the conversion of AlF_3 to AlN in the Pt–Rh tube furnace, see fig. 2. Sample P was cut from a single crystal of AlN grown by Pechiney. It was a particularly clear section almost water white in color. The crystal is the same as crystal R169 measured by Slack [92]. Sample CC was a single crystal of AlN grown by Campbell and Chang [108]. This crystal had both clear and dark blue bands in it. The spectrum given in fig. 7 is for a clear section of the crystal. The dashed line labeled edge is the extrapolated absorption edge from Yim et al. [2]. Samples P and CC probably contain both oxygen and carbon as impurities. This assumption is based on a knowledge of the way in which they were grown. Sample P actually has $3 \pm 2 \times 10^{20}$ oxygen atoms per cm^3. These two samples are not characteristic of pure AlN, but are shown for comparison.

The several W samples in fig. 7 have only oxygen as the major impurity. In addition, they may have a variable concentration of N vacancies. Impurities such as B, Be, C, Si, S, etc. have been carefully excluded. From fig. 7 it is clear that the absorption on the low energy side of the edge is extrinsic and varies from sample to sample. This result is in agreement with band structure calculations [3–5] which predict a direct band gap for AlN, and hence a sharply rising absorption edge. The two features of the extrinsic absorption are the broad band extending from $6{,}000 \leqslant \bar{\nu} \leqslant 43{,}000$ cm^{-1} and the rather sharp peak at $\bar{\nu} = 23{,}070$ cm^{-1} or 2.85 eV. One of these features is probably caused by oxygen, the other by nitrogen vacancies. If the W-2 through W-39 series is examined, and if it is assumed that the concentrarion of N vacancies is greater at the higher growing temperatures, then the height of the peak at 23,070 cm^{-1} (above background) seems to correlate with the oxygen concentration, while the magnitude of the broad background absorption correlates with the N vacancy concentration.

9. Conclusions

(1) It is possible to make high purity AlN powder from Al metal using AlF_3 as an intermediate compound. If surface oxidation of the powder is avoided, it appears to produce AlN with only 100 ppm of oxygen and lower amounts of other impurities. The purest AlN made in this laboratory has 350 ppm oxygen.

(2) Single crystals of AlN up to a few millimeters in size have been grown by gas phase transport. Both open and sealed tungsten tubes have been used. The crystals are yellow-brown or amber in color.

(3) Optical absorption studies indicate extrinsic absorption on the low energy side of the optical band gap at 6.2 eV. Some combination of oxygen impurities and nitrogen vacancies appear to be responsible for the absorption seen in the present samples.

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