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$$R_3Al + NH_3 \rightarrow R_3Al{:}NH_3 \rightarrow \rightarrow AlN + 3RH$$
$$(\text{where } R = CH_3,\ C_2H_5,\ C_4H_9,\ \text{etc.})$$

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STUDIES OF ORGANOMETALLIC PRECURSORS TO ALUMINUM NITRIDE

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ABSTRACT

The reaction of trialkylaluminum compounds with ammonia has been examined as a potential route to high purity AlN powder and to AlN thin films. This reaction proceeds in stages in which the initially formed Lewis acid/base adduct undergoes thermal decomposition to a series of intermediate alkylaluminum-amide and -imide species with increasing Al-N bonding, i.e.,

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$$(\text{where } R = CH_3,\ C_2H_5,\ C_4H_9,\ \text{etc.})$$

The structure and properties of several of these species have been studied using various physical and chemical methods, leading to a better understanding of the chemistry of this novel AlN precursor system. The structure of the intermediate organoaluminum amide, $(CH_3)_2AlNH_2$, has been determined by single crystal X-ray diffraction methods and found to contain molecular trimer units with a six-membered Al-N ring structure similar to those which make up the wurzite structure of AlN. This compound is readily volatile and has been used to deposit AlN thin films on Si surfaces by a low-pressure CVD process. This approach has also been used to prepare AlN as a high surface area, high purity powder.

INTRODUCTION

The high refractory and chemically resistant nature of aluminum nitride coupled with its large energy gap (ca. 6 eV), its high intrinsic thermal conductivity (3.2 W/cmK), its closely matched thermal expansion to silicon, and the fact that it is piezoelectric with a high acoustic wave velocity, make it an attractive prospective material for a wide range of applications in electronics, including substrates for Si-based integrated circuits as well as both passive and active components in various electronic devices (1-8). Moreover, its optical transparency throughout the visible and the near infrared (2,3) provide additional materials application opportunities. However, it is well known that small concentrations of impurities such as oxygen as well as vacancies and other defects resulting from off stoichiometry can appreciably degrade the thermal conductivity to a small fraction of the "intrinsic" value (3,7,8). These impurities can also have a significant effect on other physical properties, including the conductivity and light transparency, rendering AlN of little real value for many prospective applications unless it can be economically prepared in an exceptionally high state of purity.

The most frequently used procedures for the preparation of AlN powder involve the direct reaction of aluminum with either nitrogen or ammonia, or the carbothermal reduction of alumina in the presence of nitrogen (2,9). These methods generally yield a gray AlN powder which often contains some unreacted Al as well as high concentrations of oxygen (>1%) and other impurities. Moreover, it is difficult to control the particle size of the AlN powder, rendering consolidation to a dense ceramic by sintering or hot pressing more difficult. AlN powder of high purity has been prepared by reaction of AlF_3 (or its precursor $(NH_4)_3AlF_6$) with NH_3 gas (3,10);

however, this method requires high temperatures, is inherently costly and yields the highly corrosive HF as a byproduct.

Aluminum nitride has also been prepared in the form of thin films by various chemical and physical vapor deposition procedures including the reaction of trimethyl aluminum (TMAL) and NH_3 (11-13). This latter approach employs the reactants in the vapor state at near atmospheric pressure with hydrogen as a carrier gas. Under proper conditions, this method and various other CVD and PVD methods have been used successfully to generate both polycrystalline and epitaxial AlN thin films; however, in general, they employ substrate temperatures well in excess of 1000°C and, are therefore, inappropriate for many of the prospective applications in electronics.

The reaction of trimethyl aluminum with ammonia was apparently first studied by Wiberg in Germany during WWII and is reported in summary form in a review of WWII German Science published in 1948 (14). The basic reactions involved include the formation of a Lewis acid/base adduct between $Al(CH_3)_3$ and NH_3 and its stepwise conversion to AlN and CH_4 on heating.

$$\begin{gathered}
Al(CH_3)_3 + NH_3 \rightarrow (CH_3)_3Al{:}NH_3 \\
(CH_3)_3Al{:}NH_3 \rightarrow (CH_3)_2AlNH_2 + CH_4 \\
(CH_3)_2AlNH_2 \rightarrow CH_3AlNH + CH_4 \\
CH_3AlNH \rightarrow AlN + CH_4
\end{gathered}$$

The first reaction was carried out under unspecified conditions to yield a crystalline solid which was identified as the $(CH_3)_3Al{:}NH_3$ adduct. This adduct was found to melt at 56.7 C with the concurrent evolution of methane leading, after 1 hour heating at 70°C, to the intermediate $(CH_3)_2AlNH_2$ species, which was reported to be a dimer in liquid ammonia solution. This crystalline intermediate had an appreciable volatility (vapor pressure at 70°C = 1 mm Hg) and melted at 134.2°C. Further heating at 160 - 200°C resulted in the loss of more methane and, via a "CH_3AlNH" intermediate, eventually gave what was reported to be "pure" AlN. A detailed experimental procedure was not provided in this brief account nor was a full description of the intermediates and form of the AlN final product given. Subsequent work on organoaluminum-nitrogen compounds has focused largely on the products of the reaction of the aluminum trialkyls with organic amines and, for the most part, has not dealt with the conversion of these compounds to AlN. The apparent sole exception is a 1978 Japanese patent in which the preparation of AlN powder by pyrolysis of various organoaluminum amides and imides was claimed (15). The preferred embodiment of this method employed a reaction involving triethylaluminum, aniline and ammonia in hexane solution, followed by heating of the precipitate formed at up to 500°C to yield a gray-white powder which was identified as AlN by elemental analysis, X-ray diffraction and its infrared spectrum.

A detailed study of the TMAL + NH_3 reaction sequence was carried out in order to evaluate the possible utilization of this approach for the preparation of high purity AlN powder. This study and the subsequent investigation of the analogous reactions of the higher alkyl homologues of TMAL has resulted in a better understanding of the chemistry of the R_3Al + NH_3 system as well as the development of an improved procedure for the preparation of high purity AlN powder and a new method for the CVD of AlN films.

RESULTS AND DISCUSSION

Studies of the TMAL + NH_3 Reaction Sequence

Due to the extreme oxygen and moisture sensitivity of the alkylaluminum compounds and their ammonia reaction products, all reactions and manipulations were carried out in an inert atmosphere (N_2 or Ar) with rigorous exclusion of oxygen and water vapor. Initial studies of the reaction between TMAL and NH_3 were carried out at low temperatures (ca. -78°C) in hydrocarbon solvents by bubbling electronic grade gaseous ammonia through the cold TMAL solution. The $(CH_3)_3Al:NH_3$ adduct was obtained on evaporation of the solvent in vacuo and either used as is for subsequent reactions or recrystallized from pentane when a higher purity product was required. This white, crystalline adduct was found to melt, as previously reported, at ca. 55°C with the evolution of a molar equivalent of methane on further heating up to 70°C, as determined by weight loss measurements and analysis of the gaseous product by gas chromatography (g.c.).

This reaction was also followed by both visual observation and measurements of the pressure of a small sample of $(CH_3)_3Al:NH_3$ in a sealed Pyrex tube connected to a pressure gauge which was heated in an oil bath. The resultant pressure/temperature curve obtained (Figure 1) shows a substantial increase in pressure between ca. 60 and 75°C accompanying the observed melting and eventual re-solidification of the sample in this temperature range. The further increase in pressure observed between 75 and ca. 135°C corresponds to that expected from the inert gas equation, indicating a well-defined decomposition reaction leading to an intermediate which is stable up to 135°C. At this point the intermediate melted with a further evolution of gas up to the temperature limit of the experimental apparatus employed (ca. 170°C).

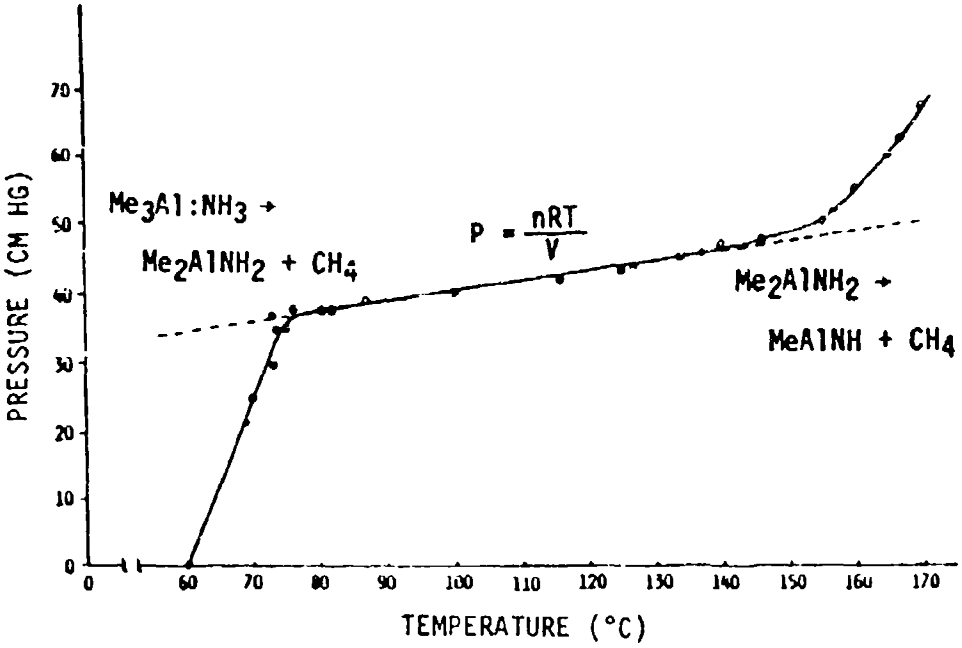

Figure 1. Changes in pressure accompanying the thermolysis of $(CH_3)_3Al:NH_3$

Separate analysis of the gas evolved on pyrolysis of the $(CH_3)_3Al:NH_3$ compound up to 300°C by g.c./mass spec showed a small amount of ethane as the only gaseous product other than methane detected. This ethane may have been formed from the dimerization of methyl radicals; however, it is more likely that it derives from the small proportion of triethylaluminum (ca. 0.4%) present in the TMAL samples used.

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The conversion of the $(CH_3)_3Al{:}NH_3$ compound to $(CH_3)_2AlNH_2$ can also be carried out in solution by maintaining the temperature of the solution above ca. 70°C. This provides a more convenient route to the $(CH_3)_2AlNH_2$ intermediate, which can be obtained simply by bubbling excess ammonia through a refluxing solution of TMAL in a solvent that boils above 70°C, such as benzene (b.p. 78°C). The product is then collected after removal of the solvent by evaporation and purified by sublimation in high vacuum.

The white, crystalline product so obtained, as reported by Wiberg, is quite volatile and readily sublimes on heating above 70°C, even at atmospheric pressure. Small amounts were heated up to 200°C, in a covered Petrie dish in a glovebox, resulting in significant loss of material by sublimation but with eventual conversion of most of the sample to an amorphous white solid of variable composition (presumably the "CH_3AlNH" intermediate reported by Wiberg). Further heating was conducted in a furnace up to 1000°C in a nitrogen atmosphere, yielding a high surface area gray-black powder which microscopic and X-ray diffraction measurements indicate is mainly AlN but with numerous black inclusions. These black inclusions are probably carbon resulting from the direct thermolysis of the last remaining fraction of $-CH_3$ groups to C and H_2 as the concentration of the N-H groups decrease and the AlN lattice becomes more rigid.

To test the possibility that this undesireable side reaction could be avoided by providing an alternative hydrogen source during this final step of the conversion, a small quantity of the powder obtained by heating the adduct up to 200°C was slowly heated (over 24 hr) to 1000°C in a furnace while passing gaseous ammonia over it. The product of this reaction was a light gray powder which was essentially free of the carbon inclusions observed in the previous sample. This product was identified as AlN by its X-ray diffraction pattern and its surface area was measured by the BET method using N_2. A value of 250 m^2/g was obtained, indicating an average particle size of around 75 A.

Preparation of High Purity AlN Powder

Due to the problems with loss of material during unconfined pyrolysis, as well as the higher cost of TMAL compared to other trialkylaluminum compounds, subsequent efforts to develop a route to high purity AlN powder have focused on the higher alkyl aluminum derivatives and, in particular, the use of triethylaluminum (TEAL) in place of TMAL in the reaction with ammonia. TEAL is currently used in large quantities in the chemical industry and is available at relatively low cost (ca. \$2.50/lb) making its use for the preparation of high purity AlN powder not only economically feasible but, in fact, competitive with current AlN prices.

The preliminary results of the investigation of the TEAL + NH_3 reaction have indicated that high surface area (ca. 40-80 m^2/g), white AlN powder of exceptional purity (O <0.3%; C = 0.06%; Si = 20 ppm; Fe and other metallic elements below detectable limits) can be obtained in essentially quantitative yield by this method. This powder picks up oxygen readily on exposure to air at ambient humidity, resulting in incorporation of over 5% O after 24 hr exposure. A small sample of this powder was hot pressed to yield a translucent specimen with a thermal conductivity of 0.8W/cmK (the oxygen content of this particular sample was ca. 2% due to exposure of the AlN powder to air on handling).

Similar results were obtained using tri-iso-butyl aluminum $[(C_4H_9)_3Al]$ in place of TEAL, which also gave a white AlN powder of high surface area and purity. In contrast to the R = CH_3 derivative, both the R = C_2H_5 and C_4H_9 systems yielded a liquid R_2AlNH_2 intermediate which was obtained on removal of the solvent under reduced pressure after addition of ammonia to the trialkylaluminum compound at room temperature.

The initial loss of alkane from the $(CH_3)_3AlNH_3$ adduct is accompanied by a sizeable exotherm (ca. 82 kJ/m by DSC); however, the apparent lack of a stable adduct with R = C_2H_5 and C_4H_9 has prevented a detailed comparison of the three systems. Differential scanning calorimetry studies of the corresponding R_2AlNH_2 compounds were carried out indicating an exothermic process for the thermolysis reaction, $R_2AlNH_2 \rightarrow RAlNH + RH$, with similar heat effects (71-83 kJ/mole) and with peak decomposition temperatures which ranged from ca. 165°C for R = CH_3 to 193°C for R = C_4H_9. The final thermolysis step, leading to AlN, is much less well-defined, occurring over a broad temperature range with no obvious heat effect evident in DSC measurements of the CH_3AlNH derivative up to 400°C. TGA studies (in flowing nitrogen at 10°C/min) indicate that most of the weight loss in this case occurs before 400°C with the last few percent occurring between 400° and 750°C; however, in the case of the R = C_2H_5 derivative, the weight loss was apparently complete by 400°C. For both systems the weight loss for the last thermolysis reaction, $RAlNH \rightarrow AlN + RH$, was close to that expected for the elimination of one mole of RH. Due presumably to the loss of starting material by volatilization or physical transfer from the TGA pan, the overall weight loss on heating to 1000°C from the R_3AlNH_3 or R_2AlNH_2 stages was somewhat greater than that expected for the elimination of the alkane.

Characterization of the $(CH_3)_2AlNH_2$ Intermediate

The high volatility of the intermediate compound, $(CH_3)_2AlNH_2$, in the TMAL + NH_3 reaction sequence suggested another possible area of application for these AlN precursors. In particular, the continuing interest in AlN thin films for a variety of prospective applications in electronics, including SAW devices operating in the high frequency region as well as electrically insulating and passivating layers for semiconductors (5,6,11-13), led to our investigation of the $(CH_3)_2AlNH_2$ compound as a potential vapor phase precursor for the chemical vapor deposition of AlN.

In order to determine the actual structure of the $(CH_3)_2AlNH_2$ species, which was reported to be a dimer by Wiberg, single crystals were grown from heptane by slow cooling of a hot, saturated solution. One of these crystals was sealed in a glass capillary and a structure determination was carried out using X-ray diffraction methods, revealing a trimeric $[(CH_3)_2AlNH_2]_3$ composition for the constituent molecules. The structure of the $[(CH_3)_2AlNH_2]_3$ trimers is illustrated in Figure 2. There is a general resemblance to the structure of the organic molecule cyclohexane, with a six-membered $(Al-N)_3$ ring in a skewed-boat arrangement and a quasi-tetrahedral arrangement of C and N about the Al atoms and H and Al around the nitrogens. These $(Al-N)_3$ rings also resemble closely the fused six-membered rings which make up the wurzite structure of AlN itself. High resolution mass spectroscopic studies of this compound indicate that these trimer molecules survive on volatilization and constitute the major species present in the gas phase.

The Possible Structure of "CH_3AlNH"

The structure of the final precursor to AlN in this series, nominally "CH_3AlNH", but of variable composition depending on the thermal history of the sample, is not yet known; however, it is likely that this insoluble species is a polymeric substance with a broad molecular weight distribution. A possible structure for this polymer can be derived from that of the $[(CH_3)_2AlNH_2]_3$ molecules by extending these rings into two-dimensional sheets of fused six-membered rings. These sheets would contain a CH_3 and a H at each internal Al and N, respectively, with additional CH_3 and H groups around the periphery of each "macromolecule". Further pyrolysis of this polymeric mixture could then lead to the further extension of the macromolecular sheets in the third dimension, resulting finally in the formation of the AlN structure.

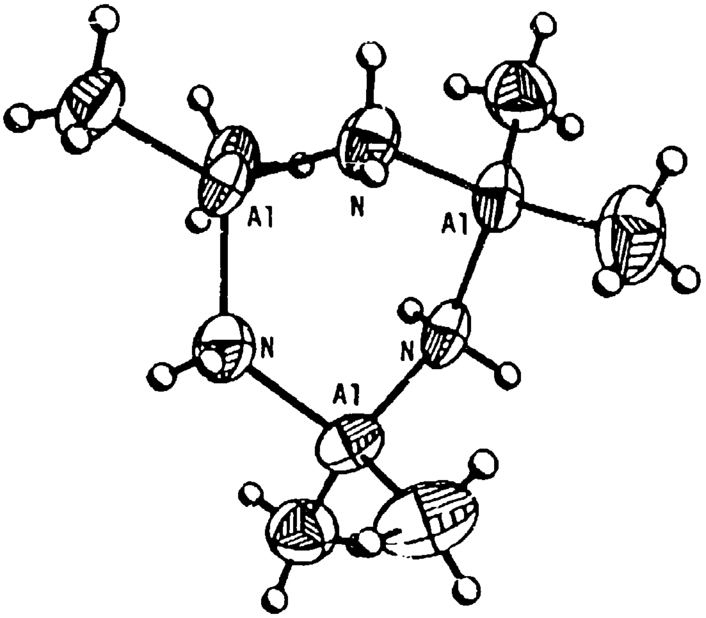

Figure 2. Ortep view of the molecular structure of $[(CH_3)_2AlNH_2]_3$.

The Chemical Vapor Deposition of AlN Using $[(CH_3)_2AlNH_2]_3$

The possibility of using the intermediate $[(CH_3)_2AlNH_2]_3$ compound as a single component precursor for the CVD of AlN films was tested by subliming a sample of the compound into an evacuated furnace tube containing Si wafer sections which was heated to 700°C. A low pressure (ca. 50 μm) was maintained in the furnace tube by continuous pumping. In this initial experiment AlN was deposited as a rough, grainy deposit on the first wafer piece, close to the entrance of the furnace. Further into the furnace the less rapid build up of AlN on the Si wafer sections resulted in progressively more fine-grained and dense deposits, which ranged from 10 to 1 μm in thickness. A micrograph of a 1 μm layer of AlN on a Si surface produced in this manner is shown in Figure 3. This apparently dense, uniform deposit was examined by TEM and found to consist of polycrystalline AlN with a typical grain size of 0.05-0.15 μm. The electron diffraction pattern gave d-spacings which could be indexed to the AlN structure. This initial experiment has been repeated several times with similar results and a systematic study of the effect of variations in the precursor sublimation rate and furnace temperature, as well as the effect of added NH_3 as a buffer gas, is in progress. Preliminary results from this study suggest that the use of ammonia has a beneficial effect on the purity of the AlN deposit and that AlN can be deposited at temperatures at least as low as 600°C.

In the context of the promising preliminary results from the CVD studies and successful development of what appears to be an economically viable approach to high purity powder, the $R_3Al + NH_3$ system holds considerable promise as a future source of AlN for applications in electronics and other areas where high purity material of controlled morphology is needed.

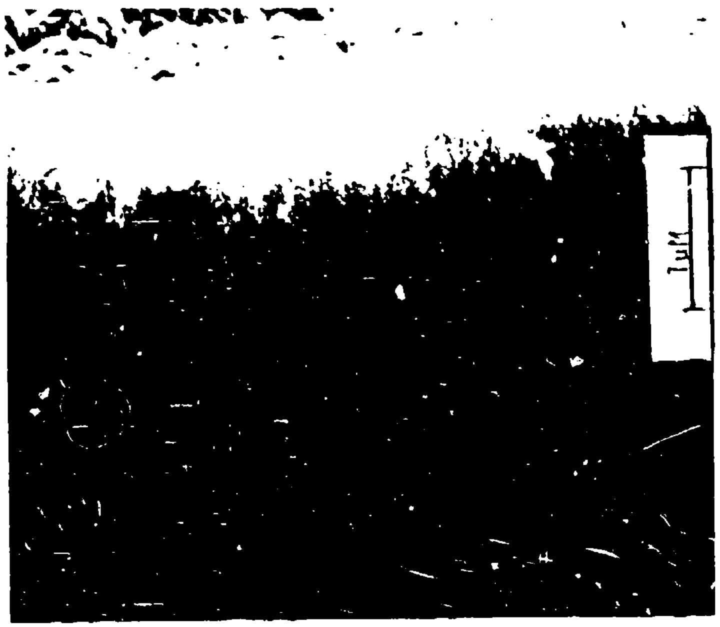

Figure 3. SEM (x 20K) of AlN deposit on Si wafer, viewed in cross-section.

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