PREPARATION OF CHEMICAL PRECURSORS TO ALUMINUM NITRIDE FROM AN AMBIENT TEMPERATURE CHLOROALUMINATE IONIC LIQUID

Michael T. Carter*, William J. Donahue and Jeffrey J. Doris

Eltron Research, Inc.
5660 Airport Blvd.
Boulder, CO 80301-2340

ABSTRACT

Heptachlorodialuminate (Al₂Cl₇) from an acidic ambient temperature ionic liquid was used to prepare precursors to aluminum nitride (AlN). The ionic liquid was a 2:1 mole ratio mixture of aluminum chloride (AlCl₃) and trimethylphenylammonium chloride (TMPAC). Al₂Cl₇ reacted exothermically with the bases ammonia (NH₃) and hydrazine (N₂H₄) to form bulk quantities of precursors to AlN. Reaction of NH₃ with the molten salt produced a mixture of ammoniate complexes, AlCl₃(NH₃)ₓ, where 1 < x < 3. Reaction with N₂H₄ produced polymers. The ammoniate was characterized by elemental analysis and FTIR spectroscopy. This precursor was used to prepare thin films of AlN by chemical vapor deposition. The films were characterized by x-ray diffraction, Auger Electron Spectroscopy and Scanning Electron Microscopy. The approach reported here demonstrates a new route to production ceramic nitride materials by exploiting highly reactive chemistry in a chloroaluminate ionic liquid.

INTRODUCTION

We have applied an acidic ambient temperature ionic liquid (molten salt) to formation of preceramic materials which can be thermally decomposed to aluminum nitride (AlN). The acidic melt was a mixture of trimethylphenylammonium chloride (TMPAC) and AlCl₃. Heptachlorodialuminate (Al₂Cl₇) in this medium reacted with ammonia to produce a preceramic material by an exothermic acid-base reaction. High reactivity of chloroacid in the molten reactant enabled formation of product at ambient temperature. The reaction produced AlCl₃(NH₃)ₓ, where 1 ≤ x ≤ 3, hereafter denoted AlCl₃(NH₃)₁₋₃. Reaction of the acidic melt with hydrazine (N₂H₄) produced polymeric products.
Thin films of AlN were deposited onto quartz and Si(111) substrates by thermal decomposition of volatile \( \text{AlCl}_3(\text{NH}_3)_3 \) by conventional chemical vapor deposition (CVD). We anticipate that the novel process reported here will form the basis for a generalized approach to controlled formation of bulk quantities of stable precursors to several important ceramic materials.

**Ambient Temperature Ionic Liquids.**

Ambient temperature ionic liquids enable convenient routes to novel chemistry and alternatives to conventional chemical solvents. They are easily handled, have essentially zero vapor pressure and dissolve a wide range of organic and inorganic solutes. Many such liquids have been identified and characterized including mixtures of \( \text{AlCl}_3 \) with \( \text{N}-\text{butylpyridinium chloride (BuPyCl)}, \) \( 1-\text{ethyl-3-methylimidazolium chloride (EMIC)} \) and \( \text{trimethylphenylammonium chloride (TMPAC)} \). These binary systems vary somewhat in electrochemical reactivity of the organic cation and phase behavior as a function of composition (i.e., mole fractions of \( \text{AlCl}_3 \)). All systems display substantial ranges of liquid composition near room temperature. Melts are prepared by mixing the two solid components which liquify with nominal formation of the organic tetrachloroaluminate:

\[
\text{RCl} + \text{AlCl}_3 \rightarrow \text{R}^+ + \text{AlCl}_4^- \quad [1]
\]

Here \( \text{R} \) represents an organic cations, for example, TMPA\(^+\), EMI\(^+\) or BPC\(^+\). The mole fraction of \( \text{AlCl}_3 \) in the melt controls distribution acids and bases at a given composition\(^4\)\(^5\) according to:

\[
2 \text{AlCl}_4^- \rightarrow \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \quad [2]
\]

for which the equilibrium constant is approximately \( 10^{-17} \) to \( 10^{-18} \) at room temperature, depending on the particular system\(^6\). At \( \text{AlCl}_3 \) mole fractions above 0.5, acidic melts containing \( \text{R}^+, \text{AlCl}_4^- \) and \( \text{Al}_2\text{Cl}_7^- \), a strong Lewis acid, are formed. The \( \text{Al}_2\text{Cl}_7^- \) mole fraction in the melt increases with \( \text{AlCl}_3 \) mole fraction. We denote melt composition as \( a:b \), where \( a \) and \( b \) are mole fractions of \( \text{AlCl}_3 \) and TMPAC in the melt, respectively. For example, a 0.6:0.4 melt contains 60% \( \text{AlCl}_3 \) and 40% TMPAC by mole fraction. The practical upper limit for the liquid range of most acidic binary melts at room temperature may be considered to be \( ca. \) 0.67:0.33.

We used the \( \text{AlCl}_3: \text{TMPAC} \) system because the organic chloride was available in bulk, commercially, at a reasonable purity. The eutectic acidic composition of this system is \( ca. \) 0.66:0.34, melting at -75°C\(^3\). Basic compositions, which melt at superambient temperatures,
Aluminum Nitride.

Aluminum nitride (AlN) features a number of outstanding properties for a variety of applications.\textsuperscript{7,8} It has high thermal conductivity and electrical resistivity. Its coefficient of thermal expansion closely matches that of silicon. For these reasons it is an attractive structural material for high power electronic applications and multichip module packaging as a heat dissipating material. Potential thin film applications exist in optoelectronics,\textsuperscript{9} harsh service environments\textsuperscript{10} and ballistic armor.\textsuperscript{11}

AlN powders are produced industrially by direct nitridation of aluminum metal or carbothermal reduction of Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{7,8,12} Direct nitridation is a high temperature process which uses finely divided, flammable and potentially explosive aluminum powder. Reduction of Al\textsubscript{2}O\textsubscript{3}, preferred for production of very fine, high purity powders, is also a high temperature process. Removal of residual carbides and oxides which compromise subsequent processing of the powder can be a problem for this method.

To address issues surrounding production of ultralow impurity materials and reduction of the extremity of process conditions, attempts have been made to use alternative methods to produce the materials or precursors. Electrochemical approaches to bulk AlN precursor synthesis, for example, have included anodic dissolution of aluminum in acetonitrile containing n-propylamine/tetrabutylammonium bromide\textsuperscript{13} and in liquid ammonia at -78°C\textsuperscript{14} to produce a polyaminoalane which may be calcined to fine AlN powder.

We realized that ambient temperature ionic liquids could realize a substantial competitive advantage by the capability to produce bulk precursor material by a relatively mild, room temperature route using simple chemistry with the capacity for scale-up. This report discusses our initial efforts to this end.

EXPERIMENTAL

**Molten Salts.**

AlCl\textsubscript{3} (Fluka) was purified by distillation from a two phase molten system of NaCl-AlCl\textsubscript{3} melt/AlCl\textsubscript{3} containing aluminum metal. Trimethylphenylammonium chloride (TMPAC, Aldrich) was dried \textit{in vacuo} to remove adsorbed water, but otherwise used as received. Molten salts were prepared by mixing appropriate amounts of AlCl\textsubscript{3} and TMPAC. The acidic eutectic composition\textsuperscript{3}, 0.67:0.33 AlCl\textsubscript{3}:TMPAC, was used throughout.
Reactions.

Reactors were assembled and filled within a Vacuum Atmospheres inert atmosphere drybox under dry nitrogen. A typical reactor was a cylindrical Pyrex vessel (500 mL) to which was fitted a removable top containing air-tight feedthroughs (Ace Glass, Inc.) for thermocouples, stirring and admission of appropriate gases. Once assembled, the reactor was transferred to a fume hood where it was connected to NH₃ (Matheson Gas Products) and N₂. The reactor was purged for 10-15 min with N₂ prior to initiation of reaction. NH₃ was added by bubbling gas into the reactor through a dispersion tube. NH₃ flow rate was not controlled. Reaction resulted in vigorous heat evolution. Melt temperature typically rose from 25 °C to >130 °C within 1 min after commencing NH₃ introduction. Therefore, the reactor was usually placed in a cold water bath to maintain temperature below 60 °C. Upon reaction completion, the reactor was purged with inert gas to remove excess NH₃ and transferred back into the drybox for harvesting of product.

Chemical Characterization of Products.

Crude product harvested from the molten salt reactor was purified by vapor phase transfer to a cold finger at 100 °C and 1 Torr static vacuum. The product was characterized by FTIR spectroscopy using a Nicolet Impact 400. Samples were pressed in KBr pellets. Neat melts were sandwiched in a thin layer between ZnSe windows. Elemental analysis of preceramic material was performed by standard methods at a commercial analytical services laboratory (Huffman Laboratories, Golden, CO). CVD films of AlN were characterized by Scanning Electron Microscopy (SEM, JEOL T-200), Auger Electron Spectroscopy (AES, Rocky Mountain Laboratories, Golden, CO) and X-ray diffractometry (Rigaku Miniflex, Cu Kα illumination).

Chemical Vapor Deposition.

CVD of AlN was performed in a reactor, shown in Figure 1, which consisted of a main quartz tube (5 cm i.d.) with hot zone ca. 10 cm long enclosed by a tube furnace. The substrate (quartz or silicon) was housed inside the tube within the hot zone. Substrates were not heated directly. The system was evacuated to 5 mTorr, then backfilled with N₂ carrier gas to an operating pressure of ca. 1-2 Torr. The precursor was vaporized at 190 °C from a pot connected by a sidearm to the main reactor, upstream of the hot zone.
RESULTS AND DISCUSSION

Typical preparative runs for reaction of acidic melt with NH$_3$ were performed with 100 mL (135 g) of 0.67:0.33 AlCl$_3$:TMPAC. Upon initiation of NH$_3$ flow into the reactor, melt temperature rose rapidly (unless cooled externally) and a white solid formed which eventually filled the reactor. After several minutes of NH$_3$ addition, heat evolution ceased, indicating exhaustive neutralization of the melt. Upon cooling to room temperature, the residual melt in the reactor solidified. This solid could be reliquified by addition of AlCl$_3$, suggesting that the residue was neutral melt (melting point, 50 °C) remaining after complete neutralization of the acidic medium by NH$_3$:

$$\text{Al}_2\text{Cl}_{7}^{-} + x \text{NH}_3 \rightarrow \text{AlCl}_3(\text{NH}_3)_x + \text{AlCl}_4^{-}$$  \[3\]

Solid product was easily removed from the reactor by skimming. Crude product was purified by vapor transfer to a cold finger at 1 Torr and 100 °C. The melting point of purified material was ca. 80 °C at 1 atm, but varied between preparative runs (especially if the melt temperature was not controlled) and exposure to the laboratory atmosphere.

Figures 2 and 3 show FTIR spectra of purified product and, for comparison, neat 0.67:0.33 AlCl$_3$:TMPAC melt, respectively. Vertical lines in Figure 2 indicate the reported positions of IR vibrations for the di- and triammoniates, AlCl$_3$(NH$_3$)$_2$ and AlCl$_3$(NH$_3$)$_3$. The corresponding spectrum of the monoammoniate was not available. Results were in good agreement with known spectra of AlCl$_3$(NH$_3$)$_2$ and AlCl$_3$(NH$_3$)$_3$. Since we could not rule out one or the other of these species, we concluded that the product was a mixture. Melt vibrational signatures, especially in the vicinity of 3000 and 1500 cm$^{-1}$, were absent from the product spectrum, indicating reasonable removal of melt impurities vapor phase transfer. Elemental analysis, shown in Table 1, did not unequivocally assign a formula to the product, but suggested a stoichiometry of AlCl$_3$(NH$_3$)$_2$ or AlCl$_3$(NH$_3$)$_3$. Based on these results, we concluded that reaction of Al$_2$Cl$_7$ with NH$_3$ produced a mixture of products, denoted AlCl$_3$(NH$_3$)$_x$, 1 ≤ x ≤ 3, or AlCl$_3$(NH$_3$)$_3$. It may be possible to control the stoichiometry of the final product during purification by vaporizing crude material in the presence of NH$_3$ pressure.

Preliminary experiments for reaction of hydrazine, N$_2$H$_4$, with Al$_2$Cl$_7$ suggested similar acid-base chemistry. Addition of hydrazine to the acidic melt resulted in formation of a solid product which was insoluble in all common solvents tested, including methanol, acetone, hexane and toluene. The FTIR spectrum of this material, shown in Figure 4, featured a broad absorption in the NH stretching region between 3000 and 3500 cm$^{-1}$, suggestive of formation of a polymer, e.g., a polyhydrazinoalane. One possible avenue for polymer formation is via a trihydrazinoalane intermediate.
Table 1. Elemental Analysis for Crude and Purified Aluminum Chloride Ammoniate Compounds, AlCl₃(NH₃)ₓ Obtained from Reaction of An Acidic Chloroaluminate Melt with Ammonia

| Element | %crude | %pure | Calc 1:1 | Calc 1:2 | Calc 1:3 | Calc 1:6 |
|---------|--------|--------|---------|---------|---------|---------|
| Al      | 12.4± 0.2 | 17 ± 2 | 17.9    | 16.1    | 14.6    | 11.5    |
| N       | 6.8     | 11.4   | 9.3     | 16.7    | 22.8    | 35.7    |
| Cl      | 53.2    | 69.4   | 70.7    | 63.5    | 57.7    | 45.2    |
| C       | 27.1 ± 0.1 | 1.7 ± 1.3 | -       | -       | -       | -       |

* %crude: atomic percent for crude product; b %pure: atomic percent for purified product; error ranges are ±20 where values from replicate determinations were available; %pure values were corrected for 6% loss of material after analysis, probably due to volatility of the AlCl₃(NH₃)ₓ adduct; c calc 1:1, calc 1:2, etc. represent theoretical atomic percent values for adducts of the

\[
\text{AlCl}_3^+ + 3 \text{N}_2\text{H}_4 \rightarrow \text{Al(NHNH}_2)_3 + 3 \text{HCl} \quad [4]
\]

\[
n \text{Al(NHNH}_2)_3 -[\text{Al(NHNH)(NHNH}_2)]-_n + n \text{N}_2\text{H}_4 \quad [5]
\]

CVD of AlN films on quartz and Si(111) substrates were performed with AlCl₃(NH₃)₁.₃. The precursor was vaporized at 190 °C from a pot connected to the main CVD reactor tube, which was maintained at ca. 1 - 2 torr. N₂ carrier gas was used at flow rate of 10 - 25 scm. XRD analysis of a film deposited on quartz at 900 °C, shown in Figure 5, agreed well with randomly oriented polycrystalline AlN. The (002) reflection was slightly stronger than expected for a completely random sample. When the substrate temperature was lowered to 850 °C, films with predominantly (002) orientation were obtained, as in Figure 6, again consistent with previous observations. Films prepared on Si(111) at 850 °C also showed strong preference for the (002) orientation and were similar to that of Figure 6, except for the presence of the Si(111) reflection. This was consistent with close lattice match between the substrate crystal face and the (002) plane of AlN. Oxide and carbide impurities were not evident in XRD patterns. SEM results showed continuous, smooth coverage of the substrate in all cases without any notable features.

Auger Electron Spectroscopy (AES) was used to evaluate elemental composition of CVD films. Figure 7 shows results for a film deposited on quartz. Ar⁺ sputtering for depth profiling was calibrated with a Ti standard. Evidence of sample charging during AES measurements indicated significant sample purity. The ratio of Al:N was close to 1:1.
verifying that AlN was the product of CVD. Oxide and carbide impurities for these samples were higher than desirable, 8 - 15 atomic %. Their absence in XRD suggested that the impurities may be amorphous. Improvements in CVD procedures will allow increased purity of the final product.

Thermal decomposition of ammoniate precursors in CVD results in generation of HCl, NH₃ and NH₄Cl, for example, by:

\[ AlCl₃(NH₃)₃ \rightarrow AlN + 3HCl + 2NH₃ \]  \hspace{1cm} [6]
\[ HCl + NH₃ \rightarrow NH₄Cl \]  \hspace{1cm} [7]

Chloride, expected to be a particularly damaging contaminant by virtue of formation of Cl⁻ donors in the aluminum nitride matrix, was absent from AES measurements. This was probably the result of performing CVD at a process temperature well above the sublimation and boiling points NH₄Cl (340 °C and 520 °C, respectively at 1 atm), which allowed complete clearance of these contaminants from the system during CVD.

CONCLUSIONS

We demonstrated that an ambient temperature ionic liquid could be used to effect solvent-free, spontaneous synthesis of a precursor to an important ceramic material. Room temperature reaction of the neat molten salt composed of AlCl₃ and TMPAC with NH₃ produced a mixture of aluminum chloride ammoniates, AlCl₃(NH₃)ₓ, where 1 ≤ x ≤ 3. The preceramic was thermally decomposed to thin films of AlN on quartz and Si(111).

The method demonstrated here showed that ambient temperature ionic liquids can play a role in production of advance materials. We are currently investigating extension of this methodology to other ceramics, for example GaN, whose importance is emerging as a wide bandgap material for optoelectronic applications. Finally, we note that the ability of ionic liquids to participate as reactants in solvent-free chemistry could have significant implications for reduction of the environmental impact of organic solvents from large scale chemical synthesis.
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Figure 1. Chemical vapor deposition system for production of thin AlN films.

Figure 2. FTIR spectrum of AlCl$_3$(NH$_3$)$_3$. Vertical lines denote reported vibrations of (-----) AlCl$_3$(NH$_3$)$_3$ and (-----) AlCl$_3$(NH$_3$)$_2$.
Figure 3. FTIR spectrum of 0.67:0.33 AlCl₃:TMPAC.

Figure 4. FTIR spectrum of reaction product between N₂H₄ and acidic melt.
Figure 5. XRD pattern for AlN deposited on quartz at 900 °C.

Figure 6. XRD of AlN deposited on quartz at 850 °C.
Figure 7. Auger electron spectroscopy depth profiling AlN deposited on quartz at 900 °C.