Rapid Solid-State Metathesis Routes to Aluminum Nitride

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Metathesis (exchange) reactions offer the possibility of controlling temperature through a judicious choice of precursors. Here, a reaction between AlCl₃ and Ca₃N₂ is found to produce phase-pure aluminum nitride (AlN) in seconds. The CaCl₂ byproduct salt, whose formation drives this highly exothermic reaction, is simply washed away after reaction completion. SEM images demonstrate that the AlN product is a micron-sized powder, while TEM shows well-formed crystallites. Thermodynamic calculations indicate that a reaction temperature of 2208 K could be reached under adiabatic conditions. Using an in situ thermocouple and a stainless steel reactor vessel to hold the precursors, a reaction temperature of 1673 K is measured 0.8 s after initiation. Switching to a thermally insulating ceramic vessel produces a maximum reaction temperature of 2010 K because of the more nearly adiabatic conditions. The high reaction temperature appears to be critical to forming phase-pure AlN. Experiments with Li₃N, instead of Ca₃N₂, produce lower temperatures (1513 K), resulting in both Al and Al₂O₃ impurities.

Introduction

Miniaturization of high-power electronic devices greatly increases the amount of thermal energy produced per unit area during their operation. This creates a need for materials that can dissipate heat rapidly to avoid electronic or mechanical failure.¹ Aluminum nitride (AlN) is an important thermal management material for silicon-based electronics because of its low coefficient of thermal expansion (4.3 × 10⁻⁶ K⁻¹), closely matching that of silicon, and its very high thermal conductivity (320 W m⁻¹ K⁻¹).² AlN is an insulator with a large band gap (E_g = 6.4 eV), high resistivity (> 10¹¹ Ω m), and low dielectric constant (8.6).³ These physical properties make AlN promising for use as an electronic substrate and as a packaging material for circuits.⁴ Other applications for AlN include UV photodetectors, pressure sensors, thermal radiation sensors, and field-effect transistors.⁵ ⁶

There is a need for new synthetic approaches to AlN and other nitrides, because most current methods are time-consuming and/or expensive. Syntheses of AlN often involve processes with complex equipment, such as ion beam evaporation⁷ or DC arc plasma, which forces aluminum ingots to react with ammonia or nitrogen gas under extreme conditions.⁷ Another synthetic method, carbothermal reduction, involves the conversion of Al₂O₃ and C in a N₂ or NH₃ atmosphere into AlN at high temperatures (> 1600 K) for several hours.⁸ Self-propagating high-temperature synthesis represents an additional route to AlN, in which Al metal powder is reacted with elemental nitrogen or NaCN at high pressures (> 1000 atm) and temperatures (up to 1900 K).⁹ One drawback to this synthesis is incomplete nitridation, especially at lower pressures. A major challenge is to obtain a high yield of pure AlN at moderate temperatures and low pressures.

Solid-state metathesis (exchange) reactions offer the advantages of a rapid, high-yield method that starts from room-temperature solids and needs little equipment. The idea behind metathesis reactions is to use the exothermicity of

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salt formation to rapidly create a desired product. A metal halide is combined with an alkali or alkaline earth main group compound to produce the desired product plus a salt that is then washed away with water or alcohol. Metathesis reactions have proven to be successful in the synthesis of a number of crystalline refractory materials including borides,10 chalcogenides,11,12 and nitrides.13–15

Once initiated, metathesis reactions reach high temperatures (>1200 K) in a fraction of a second and cool very quickly (often <5 s). Because of the rapid nature of these reactions, nucleation and growth are quickly terminated, generally resulting in small crystallites and occasionally forming metastable phases.11,16 Previous attempts to make AlN via metathesis reactions resulted in oxide impurities.17 Here, phase-pure AlN is synthesized in seconds from a metathesis reaction between Ca3N2 and AlCl3. The use of Ca3N2, which increases the temperature of the reaction, is critical to avoiding impurities. Products are characterized using powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and in situ temperature analysis.

**Experimental Section**

The precursors AlCl3 (Strem, 99.99%), Al2S3 (Cerac, 99.9%), Li3N (Cerac, 99.5%), and Ca3N2 (Cerac, 99%) were used as received. Al2S3 was formed by heating its constituent elements (Al, Cerac, 99.5%; S, Fisher) through a vapor-transport reaction in an evacuated, sealed Pyrex tube using a temperature gradient from 463 to 623 K, as modified slightly from a literature preparation of Gall18.

The synthesis of aluminum nitride was carried out in a helium-filled glovebox (Vacuum Atmospheres MO-40). The amounts of reagents were adjusted to produce 0.20 g (4.8 mmol) of AlN product. Stoichiometric amounts of the reagents were weighed and ground together with an agate mortar and pestle. The reactants were then transferred to a stainless steel (or ceramic) cup and placed within a larger capped steel reaction vessel, modeled after a bomb calorimeter.19 This allows for containment of any gases produced. The reaction is initiated through the use of a resistively heated Nichrome wire and is complete in less than a second. Precautions should be taken before performing this type of reaction, and extreme care must be used when scaling up reactions. The reaction products are then removed from the drybox and washed in 0.5 M HCl or 1.0 M H3PO4. While the aqueous washing solution removes the byproduct salt, the acid prevents base-catalyzed hydrolysis of the product.20,21 To reduce the amount of time the AlN is in the aqueous solvent, the product is immediately vacuum filtered and then dried in a furnace at 450 K. Because cellulose filter paper cannot withstand the acid washing, glass microfiber filter paper (Millipore) is used instead.

In situ reaction temperature measurements were made by modifying the stainless steel reactor. A hole was drilled through the bottom of both the steel canister and the reaction cup. A thermocouple was threaded through the hole and placed directly into the reaction mixture and secured with ceramic paste. A computer was connected to the thermocouple and programmed to record one data point every millisecond.

**Product Characterization**

Powder X-ray diffraction was performed on the washed products using a Crystal Logic θ–2θ diffractometer with a graphite monochromator and Cu Ka = 1.5418 Å radiation. The scans were taken between 10 and 1000° 2θ at 0.1° intervals with a 3-s count time. Least-squares refinement was carried out using MacDiff (http://www.geol.uni-erlangen.de/html/software/Macdiff.html) to fit the X-ray diffraction peaks and Unit Cell (http://www.esc.cam.ac.uk/ astaff/holland/UniCell.html) to then calculate the lattice parameters. In situ reaction temperatures were measured in a modified reactor with 0.03-in.-diameter C-type (Omega, 26% rhenium/84% tungsten versus 5% rhenium/85% tungsten) high-temperature thermocouples, which were placed directly into the reaction mixture. Scanning electron microscopy (SEM-Stereoscan 250) was used to characterize surface structure and particle size of the product. Transmission electron microscopy (TEM JEOL 100CX) provides a fuller picture of the morphology of the AlN crystallites. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris Diamond TG/DTA, from room temperature to 1770 K, at increments of 10 °C/min.

**Results and Discussion**

Solid-state metathesis reactions between the aluminum precursors (AlCl3 or Al2S3) and the nitriding agents (Li3N or Ca3N2) proceed in a rapid, exothermic manner upon initiation with a resistively heated Nichrome wire, as follows

\[
\text{AlCl}_3 + \text{Li}_3\text{N} \rightarrow \text{AlN} + 3\text{LiCl} \quad (1)
\]

\[
0.5\text{Al}_2\text{S}_3 + \text{Li}_3\text{N} \rightarrow \text{AlN} + 1.5\text{Li}_2\text{S} \quad (2)
\]

\[
\text{AlCl}_3 + 0.5\text{Ca}_3\text{N}_2 \rightarrow \text{AlN} + 1.5\text{CaCl}_2 \quad (3)
\]

The real driving force behind each reaction is the formation of an ionic salt (LiCl, Li2S, or CaCl2), which is so favorable that the reactions become self-propagating. The salt that is produced can then be washed away.

When choosing reagents for metathesis reactions, several important factors must be considered, including the stability of products versus reactants, the temperatures at which the precursors change phase, and the maximum reaction temperature. Clearly, the products must be considerably more stable than the reactants to create an exothermic reaction that will self-propagate. A phase change of one of the precursors is generally needed to initiate a solid-state metathesis.

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impurity most likely results from reduction of the AlCl₃ is contamination from Al metal and alumina. The aluminum moderately crystalline AlN (Figure 1, top); however, there initiated with a Nichrome wire (eq 1). This reaction produces placed in a stainless steel reactor, and the reaction was taken before washing, but Al metal is.

Changing the precursor from AlCl₃ to AlI₃ results in products and impurities similar to those found with AlCl₃. Because the melting point of AlI₃ is 461 K—versus 453 K for the sublimation temperature of AlCl₃—the reaction initiates at nearly the same temperature. A comparable $T_{\text{max}}$ is observed, along with aluminum and alumina impurities.

To achieve greater nitridation of the product, Al₂S₃ was substituted for AlCl₃. The idea is that, because Al₂S₃ has an anion with a doubly negative charge, a more stable byproduct salt, Li₂S, is expected. The $\Delta H_f$ for Li₂S is $-446.9 \text{ kJ/mol}$, compared to a $\Delta H_f$ of $-408.4 \text{ kJ/mol}$ for LiCl.²³ Aluminum sulfide was mixed and ground together with Li₃N in an agate mortar and pestle, the mixture was placed in the stainless steel reactor, and the reaction was initiated with a heated filament. The products were then removed from the He atmosphere drybox, filtered, and dried in an oven at 450 K (Figure 1, middle). The AlN produced from the reaction of Al₂S₃ and Li₃N is slightly more crystalline than that formed from AlCl₃ and Li₃N (Figure 1, top), and the Al₂O₃ impurity is eliminated. However, unwanted Al metal still presents a problem.

The persistence of metallic Al in the product at first suggested that more nitriding agent might be needed. Thus, several nitrogen-containing salts including NH₄Cl, NaN₃, and LiNH₂ were added into the reactions. As the reactions release heat after initiation, these salts decompose, and can supply either nitrogen or ammonia to aid in nitride formation.¹⁴,²⁴ However, instead of increasing the crystallinity of the nitride product, all of these additives resulted in less-crystalline products with more impurities. Adding an excess of nitride starting material also yielded only negative results. The commonality among these attempts to improve the reactions is that excess reagents act as heat sinks and lower reaction temperatures. Because this leads to less-crystalline products, a method was sought that would instead raise the reaction temperature. Aside from the possibility that AlN might simply form more readily at elevated temperatures, higher temperatures have other advantages, including more energy available to surmount activation barriers and an increased probability of reactants finding each other in the short time of reaction. Additionally, once the product forms, crystal growth will continue as long as the byproduct salt remains molten due to Ostwald ripening.²⁵,²⁶ Because hotter reactions take longer to cool, more time will be available for crystal growth, generally leading to higher crystallinity along with greater yields.

Figure 1. Powder X-ray diffraction patterns of the washed products from the following solid-state metathesis reactions that produce AlN: AlCl₃ + Li₃N (top), 0.5 Al₂S₃ + Li₃N (middle), and AlCl₃ + 0.5 Ca₃N₂ (bottom). The Miller indices (hkl) for hexagonal AlN are given in the highly crystalline pattern produced by reacting AlCl₃ with Ca₃N₂ (bottom). Aluminum (#) and alumina (*) impurities are found in the other reactions.

The synthesis of AlN was approached by considering several possible precursors, including aluminum halides or chalcogenides in combination with alkali or alkaline earth nitrates. Figure 1 shows a progression of products from a low-quality nitride contaminated with both aluminum metal and aluminum oxides to a phase-pure, high-quality nitride.

The metal chloride (AlCl₃) was chosen first because of its relatively low cost and low sublimation temperature (453 K). AlCl₃ was ground together with Li₃N, the mixture was placed in a stainless steel reactor, and the reaction was initiated with a Nichrome wire (eq 1). This reaction produces moderately crystalline AlN (Figure 1, top); however, there is contamination from Al metal and alumina. The aluminum impurity most likely results from reduction of the AlCl₃ precursor during reaction. Alumina, on the other hand, likely forms as a result of the aqueous wash, either from unreacted precursors or from hydrolysis of small, poorly formed AlN particles that are more susceptible to oxidation. Note that alumina is not observed in powder X-ray diffraction patterns taken before washing, but Al metal is.

Theoretical reaction temperatures can be calculated using the enthalpy of reaction ($\Delta H_{\text{rxn}}$), temperature-dependent heat capacities ($C_p$), and enthalpies of phase changes. The adiabatic maximum reaction temperatures, referred to as $T_{\text{max}}$, assume that reactions proceed to completion with no heat loss.

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Using Al$_2$S$_3$ but changing the nitriding agent to Ca$_3$N$_2$ was expected to achieve a higher reaction temperature with the possibility of producing AlN with enhanced crystallinity because the calcium sulfide byproduct salt is very stable ($\Delta H_f = -473.2$ kJ/mol). Unfortunately, the reaction of Ca$_3$N$_2$ and Al$_2$S$_3$ did not propagate. This is likely related to the very high melting point of the byproduct salt CaS (mp = 2524 K). Previous experiments have shown that, if the energy generated by salt formation only is insufficient to keep the salt produced in a molten state, propagation will cease. This value, called $T_{\text{max, salt}}$, was calculated for each reaction and presented in Table 1. For the reaction between Al$_2$S$_3$ and Ca$_3$N$_2$, $T_{\text{max, salt}}$ is 1202 K, well below the melting point of CaS, and therefore, it is not surprising that this reaction does not self-propagate.

The aluminum precursor was therefore changed back to AlCl$_3$ while maintaining Ca$_3$N$_2$ as the nitriding agent. The maximum adiabatic temperature predicted for the reaction of Ca$_3$N$_2$ and AlCl$_3$ is 2208 K—over 550 K above the value calculated for the reaction between Li$_3$N and AlCl$_3$. This predicted increase in reaction temperature is mainly due to the higher thermodynamic stability of the byproduct salt CaCl$_2$ ($\Delta H_f = -795$ kJ/mol) versus LiCl ($\Delta H_f = -408.4$ kJ/mol). Because the value for $T_{\text{max, salt}}$ (1427 K) is now above the melting point of the CaCl$_2$ salt byproduct (1045 K), this reaction is expected to propagate. As hoped, this reaction not only propagates rapidly but succeeds in producing single-phase, crystalline hexagonal AlN (Figure 1, bottom). A least-squares refinement of the X-ray data gives lattice parameters of $a = 3.1090$ Å and $c = 4.9749$ Å ($\pm 0.0012$ Å), which closely matches the literature values of $a = 3.1114$ Å and $c = 4.9792$ Å (JCPDS no. 25-1133). The Al content of the AlN is 48 mol % (50% expected) based on a reaction scale of 0.5Al$_2$S$_3$ + Li$_3$N $\rightarrow$ 3LiCl + AlN + 1.5CaCl$_2$. The result was an increase of over 300 K in $T_{\text{max}}$ to 2010 K. This result is much closer to the calculated adiabatic value of 2208 K. Additionally, an increase in the crystallinity of the product was observed (Figure 1, bottom). Because slower heat dissipation results in the product remaining in the molten salt matrix for longer times, more Ostwald ripening, and hence enhanced crystallinity, occurs. This, in turn, makes the AlN product more resistant to hydrolysis in water.

From the in situ temperature measurements, it appears that $T_{\text{max}} \geq 1673$ K is needed to produce phase-pure AlN via metathesis reactions. Either products formed in cooler reactions never attain enough heat to produce AlN or the low crystallinity of the AlN particles formed make them vulnerable to attack during the aqueous wash. These results explain why Ca$_3$N$_2$ is preferable to Li$_3$N as a nitriding agent for reactions with aluminum halides.

Thermal dissipation explains why the $T_{\text{max}}$ results are lower than predicted for AlCl$_3$ + Ca$_3$N$_2$ and AlCl$_3$ + Li$_3$N, but does not entirely describe the case of Al$_2$S$_3$, where in situ measurements are found to be only about one-half of the calculated adiabatic values. Because the $T_{\text{max, salt}}$ of this reaction is less than the melting point of Li$_2$S (the byproduct salt), this reaction was not expected to propagate. However, some AlN is produced through this reaction. To understand

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**Table 1.** Calculated and Measured Reaction Temperatures of AlN-Producing Solid-State Metathesis Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T_{\text{max, calc}}$ (K)</th>
<th>$T_{\text{max, exp}}$ (K)</th>
<th>$T_{\text{max, salt}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$ + 0.5Ca$_3$N$_2$ $\rightarrow$ AlN + 1.5CaCl$_2$</td>
<td>2208</td>
<td>1673</td>
<td>1427</td>
</tr>
<tr>
<td>AlCl$_3$ + Li$_3$N $\rightarrow$ AlN + 3LiCl</td>
<td>1656</td>
<td>1513</td>
<td>1503</td>
</tr>
<tr>
<td>0.5Al$_2$S$_3$ + Li$_3$N $\rightarrow$ AlN + 1.5Li$_2$S</td>
<td>2073</td>
<td>1373</td>
<td>1086</td>
</tr>
</tbody>
</table>

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**Figure 2.** In situ temperature measurements for the following AlN reactions: (a) AlCl$_3$ + 0.5 Ca$_3$N$_2$ in an insulating cup, (b) AlCl$_3$ + 0.5 Ca$_3$N$_2$, (c) AlCl$_3$ + Li$_3$N, and (d) 0.5Al$_2$S$_3$ + Li$_3$N.

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why this occurs, it is worth considering the temperatures at which the reactants change phase. AlCl₃ sublimes at approximately 453 K, whereas Al₂S₃ does not melt until 1645 K.²³,²⁸ Because the Nichrome wire detonator heats to near 1100 K when current is run through it, there is ample energy to vaporize some of the molecular solid AlCl₃, but not the extended network structure of Al₂S₃, which remains in solid form. Thus, the stability of Al₂S₃ leads to an incomplete reaction with Li₃N, while the high melting point of Li₂S (the byproduct salt) prevents self-propagation because a molten salt does not form (the melting point for Li₂S > T_max,salt). This explains why the observed T_max value is much lower than expected.

The morphologies of the products were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). An SEM image of the AlCl₃ + Ca₃N₂ reaction product is shown before (Figure 3a) and after (Figure 3b) washing in acid. Figure 3a demonstrates that, before the byproduct CaCl₂ is washed away, the product appears as a melt of CaCl₂, and (b) after acid washing, pure AlN appears as a fine micron-sized powder. The AlN product is composed of well-formed, micron-sized crystallites as imaged with TEM (Figure 4). The edges are well-defined, thus demonstrating that hydrolysis has not destroyed the surface morphology of the sample.

Conclusions

A solid-state metathesis reaction between AlCl₃ and Ca₃N₂ is shown to be a fast, reliable method for producing high-quality aluminum nitride. The driving force behind the reaction is the formation of a thermodynamically stable byproduct salt that is easily removed from the nitride product through an acid wash/filtration process. This highly exothermic reaction reaches a temperature above 2100 K within a fraction of a second and then quickly cools to room temperature. Theoretical maximum reaction temperature

calculations based on thermodynamic data and in situ temperature measurements were used to gain an understanding of these metathesis reactions. Higher sustained reaction temperatures are necessary for the formation of phase-pure AlN. At lower temperatures, incomplete nitridation leads to aluminum impurities as well as aluminum oxide, which forms upon washing. Extension of this method to produce other nitrides using Ca₃N₂ as the nitriding agent along with a thermally insulating ceramic reaction vessel is now in progress.

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