Low-Temperature Synthesis of Aluminum Nitride by Addition of Ammonium Chloride

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ABSTRACT: Aluminum nitride (AIN) is highly insulating and has a high thermal conductivity. AIN also has the advantages of being nontoxic and chemically stable. Therefore, it is a suitable sealing material for electric devices. Previous studies have shown that the addition of NH4Cl has a large influence on the formation of AIN and can effectively be used in its low-temperature synthesis without the use of special equipment. However, it has not been clarified whether NH4Cl simply promotes the reaction between Al and nitrogen or directly contributes to the nitridation reaction. In this study, which was part of a series of studies on the development of low-temperature synthesis methods for AIN, the nitridation behaviors of Al in Al–N2, Al–NH4Cl–N2, and Al–NH4Cl–He systems were determined, and the effects of the heating temperature and amount of NH4Cl on the nitridation behavior were examined in detail. When NH4Cl was added, AIN began to form at 600 °C, a formation temperature that was approximately 200 °C lower than that when only Al powder was heated under a nitrogen stream. The fact that the formation of AIN was also observed when the NH4Cl-added Al powder was heated under a helium gas stream confirmed that nitrogen derived from NH4Cl contributed to the formation of the AIN. Furthermore, based on the experimental results, the reaction mechanism was clarified, and the kinetic parameters for the nitridation of Al were determined.

INTRODUCTION

Semiconductor devices such as large-scale integrations (LSIs) and integrated circuits (ICs) are protected by highly insulating sealing materials to inhibit electrostatic breakdown due to static electricity and leakage. In recent years, to achieve both high-performance and low-cost electronic components, the miniaturization and high integration of LSIs and ICs have been promoted, but the problem of increased power consumption has become apparent. There are two types of leakage power in LSIs: standby power consumption and operation power consumption. Because the subthreshold current related to the former is highly temperature-dependent, there is a problem with the leakage current increasing in the high-temperature region. Moreover, the heat generated by semiconductor devices can cause malfunctions or thermal runaway. Therefore, to protect semiconductor devices and reduce their power consumption, sealing materials are required that are both highly insulating and thermally conductive to allow heat from a device to easily be emitted to the environment.

The use of a thermally conductive filler is believed to improve the thermal conductivity of the sealing material used for a semiconductor device. Aluminum oxide is chemically stable and harmless to the human body. Moreover, its volume resistivity is higher than 10^14 Ω·cm, while its thermal conductivity is as low as 20.5–29.3 W/(m·K).1 Beryllium oxide has excellent insulation properties (volume resistivity = 10^{15}–10^{17} Ω·cm) and an even higher thermal conductivity (250–265 W/(m·K)).1 but is a highly toxic compound. On the other hand, aluminum nitride (AIN) is highly insulating (volume resistivity >10^{14} Ω·cm) and has a high range of thermal conductivity (140–320 W/(m·K)),1 which satisfies the requirements for a sealing material. AIN also has the advantages of being nontoxic and chemically stable, and its low density favors product miniaturization. However, because the thermal conductivity of AIN decreases in the presence of impurities such as oxygen, it is necessary to synthesize high-purity AIN if it is to be used as a sealing material.

The main synthesis methods for AIN are carbothermal reduction, chemical vapor deposition (CVD), and direct nitridation. AIN synthesis by carbothermal reduction involves heat-treating aluminum oxide or aluminum hydroxide at 1400–1800 °C under a nitrogen or ammonia gas stream in the presence of carbon as a reducing agent.2–7 In this method, the heat treatment is carried out under an oxygen or air stream to remove residual carbon in a temperature range of 600–800 °C at which AIN is not oxidized. However, when the sample temperature exceeds 800 °C, as a result of the combustion heat of carbon, the purity decreases due to the oxidation of AIN.

Morgan et al.8 proposed a method for synthesizing AIN by heating a boric acid added sample in nitrogen. However, although the addition of boric acid is suitable for the synthesis of AIN for refractory applications, it is unsuitable for synthesizing a sealing material for use in electronic and optical devices because boron nitride remains in the prepared AIN. In the CVD method, AlCl3 is nitrided with nitrogen gas or ammonia at 1400–1800 °C to obtain AIN, but precise control is required, such as vacuum conditions.9–12 On the other hand, in the direct nitridation method, a sample prepared...
by adding alkali fluoride, alkali chloride, or sodium nitrite to Al powder is heated at 650 °C, which is slightly lower than the melting point of aluminum, and then the nitridation of aluminum is conducted by increasing the heating temperature.\textsuperscript{12–21} Selvaduray and Sheet\textsuperscript{13} performed the latter heating stage at 1600 °C for stabilization. Qiu and Gao\textsuperscript{14,15} reported that the addition of KCl and NH\textsubscript{4}Cl lowered the nitridation temperature, and the diffusion of NH\textsubscript{3} gas into the solid was accelerated by the generation of voids formed by the volatilization of KCl. Radwan and co-workers\textsuperscript{16,17} reported that the addition of NH\textsubscript{3} gas was used.\textsuperscript{18} The synthesis of AlN with NH\textsubscript{4}Cl has previously been reported. When AlCl\textsubscript{3} and NH\textsubscript{3} at 453 K and then heating the AlCl\textsubscript{3}·NH\textsubscript{3} remained when nitrogen was used.\textsuperscript{18} The synthesis of AlN with NH\textsubscript{4}Cl has previously been reported. When NH\textsubscript{4}Cl is used in the production of AlN, it may promote the reaction of Al with N\textsubscript{2}(g) and act as a nitrogen source. However, the reaction mechanism of Al and NH\textsubscript{4}Cl has not been clarified.

In the present study, the nitridation behavior of Al was investigated following heat treatment with and without NH\textsubscript{4}Cl under N\textsubscript{2} and helium (He) atmospheres. The effects of the heating temperature and amount of NH\textsubscript{4}Cl on the nitridation behavior were examined in detail. Furthermore, the nitridation reaction mechanism was clarified based on the experimental results, and a kinetic analysis was conducted to determine the kinetic parameters related to the formation of AlN.

\section*{RESULTS AND DISCUSSION}

\textbf{Formation of AlN in the Al–N\textsubscript{2} System.} Figure 1 shows the change in the AlN yield ($\alpha$) with the reaction

\begin{equation}
\text{Al} + 0.5\text{N}_2(g) \rightarrow \text{AlN}
\end{equation}

Figure 1. Change in AlN yield, $\alpha$, with temperature under N\textsubscript{2} stream.

$\alpha = (W_{\text{obs}} - W_{\text{init}})/(W_{\text{theo}} - W_{\text{init}}) \times 100\%$

where $W_{\text{init}}$ and $W_{\text{obs}}$ are the weights of the sample before and after heat treatment, respectively, and $W_{\text{theo}}$ is the theoretical weight assuming that the Al is completely converted to AlN. The nitridation of Al began at approximately 800 °C where it was observed that the Al powder started to melt. The nitridation reaction proceeded rapidly from approximately 900 °C, and the $\alpha$ value reached 83% at 1000 °C. Radwan and co-workers reported that an outer shell of AlN was formed on the surfaces of the Al particles at the initial stage of the nitridation reaction, and then the internal pressure increased with the temperature as a result of the melting of the unreacted Al. This led to the Al melt leaking out of the shell.\textsuperscript{16,17} The drastic increase in the AlN yield at approximately 900 °C confirmed in this study was presumably due to the nitridation of unreacted Al accompanying the collapse of the AlN shell. When the heat treatment was carried out at 1000 °C for 1 h, the $\alpha$ value further increased to 88%. Figure 2 shows the X-ray diffraction patterns of samples prepared by heating Al powder at temperatures from 700 to 1000 °C without any additive.

\textbf{Effect of NH\textsubscript{4}Cl Amount on AlN Formation in the Al–NH\textsubscript{4}Cl–N\textsubscript{2} System.} Samples with 30–70 wt % NH\textsubscript{4}Cl were heated under nitrogen streams at 1000 °C for 1 h. Figure 3 shows the X-ray diffraction patterns of the nitrided samples produced in the Al–NH\textsubscript{4}Cl–N\textsubscript{2} system. The addition of NH\textsubscript{4}Cl promoted the nitridation of Al compared to the sample heated in the Al–N\textsubscript{2} system shown in Figure 2. In particular, in the sample containing 70 wt % NH\textsubscript{4}Cl, the unreacted Al completely disappeared. The NH\textsubscript{4}Cl/Al molar ratio of the sample with 70 wt % NH\textsubscript{4}Cl was 1.17, whereas the samples with 30–60 wt % NH\textsubscript{4}Cl had small NH\textsubscript{4}Cl/Al ratios of 0.22–0.76. An NH\textsubscript{4}Cl/Al molar ratio greater than one was confirmed to be desirable for the complete nitridation of Al. In the Al–NH\textsubscript{4}Cl system, high-purity AlN could be synthesized under the following conditions: NH\textsubscript{4}Cl amount, 70 wt %; reaction temperature, 1000 °C; time, 1 h. Qiu and Gao prepared AlN by heating a mixture of Al, NH\textsubscript{4}Cl, and KCl.
at 1000 °C for 5 h.14,15 In comparison, with our Al−NH4Cl system, AlN could be synthesized in a much shorter reaction time.

Figure 4 shows the changes in appearance of the samples with 30−70 wt % NH4Cl after heating at 1000 °C for 1 h under nitrogen stream. When the NH4Cl amount was less than 60 wt %, the color of the product was dark gray, whereas the product obtained from the 70 wt % sample was a light grayish white and clearly aggregated. This is evidence that the sample melted once during the heat treatment of the NH4Cl-added sample. An enlarged scanning electron microscopy (SEM) image showed that the aggregate consisted of uniform AlN particles. The average particle size of the AlN was 1.8 μm, and the particles ranged in size from 1.6 to 2.2 μm.

Effect of Reaction Temperature on AlN Formation in the Al−NH4Cl−N2 System. Samples with 70 wt % NH4Cl were heated under nitrogen to temperatures ranging from 500 to 1000 °C for 1 h. The X-ray diffraction patterns of the obtained samples are shown in Figure 5. AlN peaks are observed at 600 °C, which indicate that the AlN formation temperature decreased by approximately 200 °C compared to that when only Al powder was heated under a nitrogen stream. When the reaction temperature was further increased to 900 °C, the full conversion of Al to AlN was achieved, as observed by the absence of the peaks corresponding to the unreacted material.

Role of NH4Cl in the Formation of AlN. The distribution of elements changed with the temperature in the Al−NH4Cl−N2 system. Samples with 70 wt % NH4Cl were heated under nitrogen to temperatures ranging from 500 to 1000 °C for 1 h. The resulting element distributions in the nitrided samples are listed in Table 1. The weight of the sample, which was the sum of the Al, N, H, and Cl (indicated by circles), decreased to 22.9% for the 600 °C sample and subsequently increased for samples heated at temperatures over 700 °C. The weight loss for the 600 °C sample was presumed to be due to the volatilization of NH4Cl, which has a sublimation temperature of 338 °C, as described in eq 3.

\[ \text{NH}_4\text{Cl} \rightarrow \text{NH}_3(g) + \text{HCl}(g) \]  

Figure 6 shows the thermodynamic equilibrium calculations for the (a) Al and (b) N, H, and Cl chemical forms in the heat treatment of NH4Cl under an inert atmosphere using HSC chemistry (Outokumpu, ver. 5.0). Figure 6 shows that AlN can be obtained from a reaction between Al and NH4Cl at temperatures below 100 °C. Although the amount of AlN decreases at 100−300 °C where Al2Cl6(g) is stable, the amount of AlN increases at temperatures above 300 °C. Because the direct nitridation of Al with NH4Cl at temperatures below 100 °C, which is a solid−solid reaction, did not occur dynamically, as shown in Figure 5, it is estimated that AlN could be formed through the reaction of Al with N2(g) and/or NH3(g) derived from the decomposition of NH4Cl, as shown in eqs 1 and 4. A decrease in the Al content is observed at 600 °C in Table 1, which is presumed to be due to the volatilization of AlCl3(g), as shown in the thermodynamic calculation (Figure 6). AlCl3 has a sublimation temperature of 183 °C and is formed according to eq 5.

\[ \text{Al + NH}_3(g) \rightarrow \text{AlN} + 1.5\text{H}_2(g) \]  

\[ \text{Al + 3HCl(g) \rightarrow AlCl}_3(g) + 1.5\text{H}_2(g) \]  

Table 1. Changes in Elemental Distributions of Samples in the Al−NH4Cl−N2 System

| temperature (°C) | (wt %, raw sample basis) | Al | N | H | Cl | unknown |
|------------------|--------------------------|----|---|---|----|---------|
| (raw sample)     | 30.0                     | 18.3 | 5.2 | 46.5 | 0 |
| 700              | 17.5                     | 4.6  | 0  | 0   | 2.2 |
| 800              | 17.6                     | 7.8  | 0  | 0   | 0.5 |
| 900              | 18.1                     | 8.4  | 0  | 0   | 0.5 |
| 1000             | 15.9                     | 8.1  | 0  | 0   | 0.4 |

Figure 5. XRD patterns of samples synthesized at temperatures from 500 to 1000 °C for 1 h with 70 wt % NH4Cl.

Table 1. Changes in Elemental Distributions of Samples in the Al−NH4Cl−N2 System

| temperature (°C) | (wt %, raw sample basis) | Al | N | H | Cl | unknown |
|------------------|--------------------------|----|---|---|----|---------|
| (raw sample)     | 30.0                     | 18.3 | 5.2 | 46.5 | 0 |
| 700              | 17.5                     | 4.6  | 0  | 0   | 2.2 |
| 800              | 17.6                     | 7.8  | 0  | 0   | 0.5 |
| 900              | 18.1                     | 8.4  | 0  | 0   | 0.5 |
| 1000             | 15.9                     | 8.1  | 0  | 0   | 0.4 |

Figure 3. XRD patterns of samples synthesized at 1000 °C for 1 h with additions of NH4Cl from 0 to 70 wt %.

Figure 4. Changes in appearances of samples with 30−70 wt % NH4Cl after heating at 1000 °C for 1 h under nitrogen stream.
The Gibbs free energy values for the decomposition of NH₄Cl and formation of AlN are shown in Figure 7. The nitridation of Al by N₂(g) and NH₃(g) according to eqs 1 and 4 is presumed to occur in the entire temperature range from 0 to 1000 °C. Because the Gibbs free energy of the formation of NH₃(g) from NH₄Cl according to eq 3 shows a negative value at temperatures greater than 380 °C, NH₄Cl is decomposed into NH₃(g) and HCl(g) after sublimation at 338 °C, and the decomposition gases influence the formation of AlN and loss as AlCl₃.

A small amount of nitrogen was observed in the sample heat-treated at 600 °C. Based on the XRD pattern in Figure 5, this nitrogen is considered to be in the form of AlN. On the other hand, the increase in nitrogen content observed in the temperature range of 600–800 °C indicates the formation of AlN by the reaction of Al and nitrogen because the NH₄Cl has already disappeared by 600 °C, as shown in Figure 5.

**Origin of the Nitrogen in AlN Prepared with the Al–NH₄Cl–He System.** Samples with 70 wt % NH₄Cl were heated under helium to temperatures ranging from 600 to 1000 °C for 1 h, and the formation of AlN was examined. Figure 8 shows the change in the X-ray diffraction patterns of the samples with temperature in the Al–NH₄Cl–He system. Only peaks attributed to Al and NH₄Cl were observed at 600 °C, whereas the formation of AlN was confirmed at 700 °C. Because the peak intensity of the AlN did not change in the range of 700–1000 °C, the nitridation of Al with NH₄Cl occurred at approximately 700 °C.

Table 2 indicates the changes in the distribution of elements with the reaction temperature for the samples prepared using the Al–NH₄Cl–He system. Because negligible changes in the amounts of Al and N were observed, the formation of AlN with the NH₃(g) derived from the decomposition of NH₄Cl, as shown in eq 6, was considered to be complete at temperatures between 600 and 700 °C.

$$\text{Al} + \text{NH}_3(g) \rightarrow \text{AlN} + 1.5\text{H}_2(g)$$  (6)

It was confirmed that the origin of the nitrogen in the AlN in the Al–NH₄Cl–He system was NH₄Cl, whereas the nitrogen in the Al–NH₄Cl–N₂ system came from both NH₄Cl and the nitrogen gas. Therefore, the amount of nitrogen in the AlN derived from the nitrogen gas could be calculated from the difference in the nitrogen contents listed in Tables 1 and 2.

**Table 2. Changes in Elemental Distributions of Samples in the Al–NH₄Cl–He System**

| temperature (°C) | Al (wt %) | N (wt %) | H (wt %) | Cl (wt %) | unknown (wt %) |
|------------------|-----------|----------|----------|-----------|----------------|
| (raw sample)     | 30.0      | 18.3     | 5.2      | 46.5      | 0              |
| 700              | 16.5      | 2.3      | 0        | 0         | 2.2            |
| 800              | 16.0      | 2.6      | 0        | 0         | 1.6            |
| 900              | 16.0      | 3.0      | 0        | 0         | 0.7            |
| 1000             | 16.1      | 3.5      | 0        | 0         | 0.8            |

**Effect of NH₄Cl Addition on AlN Yield.** Figure 9 shows a comparison of the yields of AlN (α) formed during the heat treatment of samples with and without NH₄Cl in the temperature range of 700–1000 °C for 1 h. The amount of
NH₄Cl was set at 70 wt %. Because α could not be directly evaluated from the weight change, it was calculated from the aluminum and nitrogen contents according to eq 7

$$\alpha = \frac{W_N}{W_A} \times \frac{(N_N/N_A)}{100}$$

where $W_N$ and $W_A$ are the contents of nitrogen and aluminum in the sample, respectively, and $N_N$ and $N_A$ are the atomic weights of nitrogen and aluminum, respectively. The value of $\alpha$ reached 50, 84, and 89% in the Al–NH₄Cl–N₂ system at 700, 800, and 900 °C, respectively, which confirmed that the addition of NH₄Cl allowed the synthesis temperature of AlN to be effectively lowered. Radwan and co-workers reported that when a sample with 50% NH₄Cl was heated at 1000 °C for 1 h in a nitrogen stream, a high nitridation extent of 95% was obtained, but unreacted Al remained.¹⁶,¹⁷ In this study, the nitridation extent reached 98%, and no unreacted Al was observed after the heat treatment of the sample with 70 wt % NH₄Cl at 1000 °C for 1 h. Thus, it was confirmed that increasing the amount of NH₄Cl was effective at achieving complete nitridation.

**Kinetic Analysis of AlN Synthesis.** It has been shown that the nitridation of Al in the Al–N₂ system proceeds according to the reaction outlined in eq 4, whereas for the Al–NH₄Cl–N₂ system, the reactions in eqs 1, 3, 4, and 5 take place. It was assumed that the reaction rate $r_i$ ($i = 1, 3–5$) of each reaction could be expressed as a first order in the amount of each compound, as shown in eqs 8–13, and that the reaction rate constant of each reaction had an Arrhenius-type temperature dependence, as shown in eq 13.

$$d[\text{NH}_4\text{Cl}]/dt = -r_1 = -k_1[\text{NH}_4\text{Cl}]$$
$$d[\text{HCl}(g)]/dt = r_3 = k_3[\text{Al}][\text{HCl}(g)]$$
$$d[\text{NH}_3(g)]/dt = r_3 = k_3[\text{Al}][\text{NH}_3(g)]$$
$$d[\text{Al}]/dt = -r_4 = r_5$$
$$r_5 = -k_4[\text{Al}] - k_5[\text{Al}][\text{NH}_3(g)] - k_6[\text{Al}][\text{HCl}(g)]$$
$$d[\text{AlN}]/dt = r_1 + r_4 = k_3[\text{Al}][\text{NH}_3(g)]$$

$$k_i = k_{i,0} \exp(-E_i/RT)$$

where $k_i$, $k_{i,0}$, and $E_i$ ($i = 1, 3–5$) are the reaction rate constant, frequency factor, and apparent activation energy of each reaction, respectively. The simultaneous differential equations for the mass balance of each compound were solved using the Runge–Kutta–Gill algorithm, and the kinetic parameters, $k_{i,0}$ and $E_i$ which could represent the experimental data, were determined. The initial condition of the calculation is shown in eq 14.

$$[\text{Al}]_0 = 1 \text{ mol}, [\text{NH}_4\text{Cl}]_0$$
$$= 0(\text{Al–N}_2\text{system}) \text{ or } 1.18$$
$$\text{mol}(\text{Al–NH}_4\text{Cl–N}_2\text{system}),$$
$$[\text{AlN}]_0 = [\text{AlCl}_3(g)]_0 = [\text{HCl}(g)]_0$$
$$= [\text{NH}_3(g)]_0 = 0 \text{ mol}$$

Figure 11 shows the results of simulations of the formation of AlN in the Al–N₂ and Al–NH₄Cl–N₂ systems, with the derived kinetic parameters listed in Table 3. The apparent
when the NH4Cl-added Al powder was heated under a helium/nitrogen stream. The formation of AlN was also observed.

The formation of AlN was measured with a thermocouple to control the reaction temperature of the outer wall of the reaction tube was determined to be 9.1 °C.

The Al powder (99.9%, EP, Nacalai Tesque) and NH4Cl (99.5%, EP, Nacalai Tesque) were used without purification. Al and NH4Cl were mixed using a mortar and then used in the nitridation experiments. The weight ratio of NH4Cl in the mixture was varied between 30 and 70 wt %. An additive was investigated in detail to develop a low-temperature synthesis process for AlN. White AlN, which was free of unreacted Al, could be synthesized by adding 70 wt % NH4Cl to the starting Al powder and heating the mixture at 1000 °C for 1 h. With the NH4Cl addition, AlN started to form at 600 °C lower than that when only Al powder was heated under a nitrogen stream. The formation of AlN was also observed when the NH4Cl-added Al powder was heated under a helium gas stream, which confirmed that the nitrogen derived from NH4Cl contributed to the formation of AlN. The reaction mechanism was estimated based on these experimental results, and the formation behaviors of AlN in the Al–N2 and Al–NH4Cl–N2 systems were successfully simulated.

### MATERIALS AND METHODS

**Samples.** The Al powder (99.9%, EP, Nacalai Tesque) and NH4Cl (99.5%, EP, Nacalai Tesque) were used without purification. Al and NH4Cl were mixed using a mortar and then used in the nitridation experiments. The weight ratio of NH4Cl in the mixture was varied between 30 and 70 wt %. An image analysis determined that the average particle size of the Al powder was 9.1 μm, with all of particles in the size range of 7.0–16.0 μm.

Nitridation. Figure 12 shows a schematic diagram of a horizontal fixed-bed reactor with a fused-silica tube (1000 mm in length, 21 mm i.d.). A horizontal tubular furnace (EKR-16K, Isuzu Seisakusho Co.) was used as the heating apparatus. The temperature of the outer wall of the reaction tube was measured with a thermocouple to control the reaction temperature. The mixture of Al and NH4Cl was contained in an alumina boat (width × height × length: 16 × 12 × 80 mm), which was placed at the center of the heating section. A 500 mL NTP/min flow of nitrogen or helium was supplied to the reactor, which was heated at a rate of 15 °C/min to the desired final temperature (500–1000 °C) and held for 1 h at that temperature. After the heat treatment, the sample was immediately cooled to room temperature. In order to investigate the role of nitrogen in the formation of AlN, the heat treatment of Al powder alone was carried out under a nitrogen gas stream.

**Analysis.** The products formed in the nitridation process were determined using an X-ray diffraction (XRD) analyzer (Ultima IV, Rigaku). The experimental conditions of the XRD measurements were as follows: CuKα radiation; tube voltage/current, 40 kV/40 mA; scan rate, 10°/min.

The sample was dissolved as described below, and the Al content in the solution was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES; SPS-5510, Seiko Instruments). The sample was completely dissolved using the selective dissolution method proposed by Yabuki et al.22 The sample (1 g) was added to a sodium hydroxide solution (100 mL, 2 mol/L) and agitated at temperatures from 80 to 90 °C for 90 min after which hydrochloric acid (50 mL, 6 mol/L) was added, and the solution was agitated for 20 min.

The nitrogen content was determined according to the analytical method JIS R1675 (methods for chemical analysis of fine aluminum nitride powders for fine ceramics).22 Ammonia gas, which was generated by the steam distillation of the sample, was reacted with an amide sulfate solution, and then the nitrogen content of the sample was determined by the neutralization titration of the solution with a sodium hydroxide solution.

### CONCLUSIONS

The mechanism for the nitridation of Al using NH4Cl as an additive was investigated in detail to develop a low-temperature synthesis process for AlN. White AlN, which was free of unreacted Al, could be synthesized by adding 70 wt % NH4Cl to the starting Al powder and heating the mixture at 1000 °C for 1 h. With the NH4Cl addition, AlN started to form at 600 °C lower than that when only Al powder was heated under a nitrogen stream. The formation of AlN was also observed when the NH4Cl-added Al powder was heated under a helium gas stream, which confirmed that the nitrogen derived from NH4Cl contributed to the formation of AlN. The reaction mechanism was estimated based on these experimental results, and the formation behaviors of AlN in the Al–N2 and Al–NH4Cl–N2 systems were successfully simulated.

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K.S. designed the experiments. K.S. and T.K. conducted the experiments and analyzed the results. T.K. wrote the paper with K.S.

**Notes**
The authors declare no competing financial interest.

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