Formation Process of Aluminium Nitride by the Vapor-phase Reaction of Aluminium Trichloride with Ammonia

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Synopsis. The reaction products of gaseous $AlCl_3$ with ammonia were $AlCl_3 \cdot 3NH_3$ at 200—500 °C, AlN, $AlCl_3 \cdot 3NH_3$, NH_4Cl at 550—900 °C, and AlN, NH_4Cl at 1000 °C. AlN is considered to be formed by the reaction of gaseous $AlCl_3 \cdot 3NH_3$, formed by the reaction of gaseous $AlCl_3$ with ammonia, with ammonia above *ca.*550 °C.

The properties of aluminium nitride (AlN) suggest that AlN has potential applications in electronic devices for high-temperature operations. AlN has become of interest as a piezoelectric film material. Concerning the deposition of AlN from aluminium trichloride ($AlCl_3$) by the vapor-phase reaction, Chu *et al.*[1] have reported the epitaxial growth of AlN by the reaction of gaseous $AlCl_3$ with ammonia. Bauer *et al.*[2] have studied the dependence of the AlN deposition rate on the conditions of the vapor-phase reaction of $AlCl_3$ with ammonia and the properties of the AlN films formed. Arnold *et al.*[3] have examined the yields of AlN films by the vapor-phase reaction of $AlCl_3$ with ammonia under various reaction conditions and estimated that the decomposition of $AlCl_3$–NH_3 adduct, formed in the reaction process, significantly contributes for the formation of AlN. However, the formation process of AlN by the vapor-phase reaction of $AlCl_3$ with ammonia has not been revealed. In this paper, the reaction products of gaseous $AlCl_3$ with ammonia at 200—1000 °C were examined. Also, the possible reactions which were considered to occur during the reaction process were examined. From these results, the formation process of AlN by the vapor-phase reaction of $AlCl_3$ with ammonia is discussed.

Experimental

The $AlCl_3$ used was prepared by the reaction of pure aluminium (Al 99.99%) with chlorine at 400 °C.[4] The chemical analysis gave Al, 20.2; Cl, 79.8% (calcd for $AlCl_3$: Al, 20.24; Cl, 79.76%). The ammonia was dried by passing it over sodium hydroxide granules and barium oxide powders.

Experimental apparatus and procedures for examining the reaction products of gaseous $AlCl_3$ with ammonia are the same as those described in the previous paper.[5] Gaseous $AlCl_3$ was formed by heating solid $AlCl_3$ (10 g) at 165 °C and was carried by a stream of argon (50 cm^3/min) into the reaction zone. The mean flow-rate of gaseous $AlCl_3$ was 6.0 cm^3 Al_2Cl_6(g)/min. Ammonia was simultaneously introduced at a flow-rate of 100 cm^3/min into the reaction zone through a separate tube. The reaction was allowed to proceed for 2 h.

The aluminium, chlorine and ammonia contents of the $AlCl_3$–NH_3 adduct formed were determined by chelatometric titration,[6] gravimetric method as AgCl, and the Kjeldahl method, respectively, after dissolving the sample in 3M-nitric acid. Thermogravimetry (TG) of the $AlCl_3$–NH_3 adduct was performed by using a thermal balance with a quartz helix (the sensitivity: approximately 113 mm/g). The sample (0.2 g) was heated at a rate of 2.5 °C/min and the flow-rate of ammonia or argon was maintained at 50 cm^3/min.

Results and Discussion

The products formed by heating gaseous $AlCl_3$ in an ammonia stream at various temperatures were examined by both X-ray analysis[7,8] and chemical analysis.

The products formed at 200—500 °C showed the same X-ray diffraction pattern, which was clearly different from those of known aluminium compounds. From the chemical analysis of the products at 200—500 °C, the ratios of Al:Cl:NH_3 of the products were calculated to be 1:3.00:3.06—3.35. As will be described later, it was found that the products absorbed ammonia. From these results, the removal of the ammonia absorbed by heating the product in an argon stream was examined by using the thermal balance. The result showed that the ammonia absorbed into the products was removed by heating the products in an argon stream at 150 °C for 3 h. A typical chemical analysis of the products formed at 200—500 °C after the removal of the ammonia absorbed gave Al, 14.6; Cl, 57.6; NH_3, 27.6%. The ratio of Al:Cl:NH_3 was calculated to be 1:3.00:3.00. From the results, it was considered that the products formed at 200—500 °C had a composition of $AlCl_3 \cdot 3NH_3$ (calcd for $AlCl_3 \cdot 3NH_3$: Al, 14.63; Cl, 57.67; NH_3, 27.70%).

The reaction products of gaseous $AlCl_3$ with ammonia at various temperatures above 200 °C are summarized in Table 1. Unreacted $AlCl_3$ was not observed throughout the temperature range of this work.

To elucidate the reaction process of gaseous $AlCl_3$ with ammonia, the behavior of the $AlCl_3 \cdot 3NH_3$, which had been formed during the reaction process, on heating in an ammonia stream was examined.

Table 1. Reaction products of gaseous $AlCl_3$ with ammonia at various temperatures

Temp/°C	Products	
	In the reaction zone	Outside the reaction zone
200—300	$AlCl_3 \cdot 3NH_3$	$AlCl_3 \cdot 3NH_3$
350—500	—	$AlCl_3 \cdot 3NH_3$
550—650	AlN (6—28)	$AlCl_3 \cdot 3NH_3$; NH_4Cl
700—900	AlN (42—82)	AlN, $AlCl_3 \cdot 3NH_3$; NH_4Cl
1000	AlN (86)	AlN; NH_4Cl

Note: the values in parentheses are mole percentages of gaseous $AlCl_3$ converted to AlN.

Table 2. Reaction products of gaseous $AlCl_3 \cdot 3NH_3$ with ammonia at various temperatures

Temp/°C	Products	
	In the reaction zone	Outside the reaction zone
500	—	$AlCl_3 \cdot 3NH_3$
550—650	AlN (6—33)	$AlCl_3 \cdot 3NH_3$; NH_4Cl
700—800	AlN (58—82)	AlN, $AlCl_3 \cdot 3NH_3$; NH_4Cl
900	AlN (85)	AlN; NH_4Cl

Note: the values in parentheses are mole percentages of gaseous $AlCl_3 \cdot 3NH_3$ converted to AlN.

The result of TG of $AlCl_3 \cdot 3NH_3$ in an ammonia stream showed that $AlCl_3 \cdot 3NH_3$ gradually absorbed ammonia at room temperature. The weight gain due to the absorption of ammonia reached a constant value after about 5 h. By heating the sample after the absorption, it lost weight gradually above about 60 °C, and the weight decreased markedly above about 230 °C. The weight loss reached 100% above about 370 °C. Vaporization of $AlCl_3 \cdot 3NH_3$ was observed during the weight loss above 230 °C. To obtain more detailed information on the behavior of $AlCl_3 \cdot 3NH_3$ on heating in an ammonia stream, $AlCl_3 \cdot 3NH_3$ (1.0 g) in a quartz boat was placed in a straight reaction tube. Ammonia was introduced into the reaction tube at a flow-rate of 100 cm^3/min. The sample part was then placed in the centre of an electric furnace maintained at a specified temperature for 1 h. The products obtained inside and outside the boat were examined. The results indicated that $AlCl_3 \cdot 3NH_3$ vaporized in an ammonia stream and that the percentage of the vaporized $AlCl_3 \cdot 3NH_3$ was 0% at 200 °C, <1% at 230 °C, 1% at 250 °C, 9% at 280 °C, 48% at 300 °C, and 100% at 320 and 350°C.

The reaction of gaseous $AlCl_3 \cdot 3NH_3$ with ammonia was then examined under similar experimental conditions for examining the reaction products of gaseous $AlCl_3$ with ammonia, described before. Gaseous $AlCl_3 \cdot 3NH_3$ was formed by heating solid $AlCl_3 \cdot 3NH_3$ in a stream of ammonia (50 cm^3/min) at 330 °C and was introduced into the reaction zone. The mean flow-rate of $AlCl_3 \cdot 3NH_3$ was 9.0 cm^3/min. The reaction products of gaseous $AlCl_3 \cdot 3NH_3$ with ammonia at various temperatures are shown in Table 2.

The results showed that the reaction of gaseous $AlCl_3 \cdot 3NH_3$ with ammonia occurred above about 550 °C to form AlN and NH_4Cl.

From the above-mentioned experimental results, the formation process of AlN by the vapor-phase reaction of $AlCl_3$ with ammonia can be represented as follows: The reaction of gaseous $AlCl_3$ with ammonia to form $AlCl_3 \cdot 3NH_3$ occurs first. Above about 550 °C, the gaseous $AlCl_3 \cdot 3NH_3$ reacts with ammonia to form AlN.

References

1) T. L. Chu, D. W. Ing, and A. J. Noreika, *Solid-State Electron.*, **10**, 1023 (1967).
2) J. Bauer, L. Biste, and D. Bolze, *Phys. Status Solidi A*, **39**, 173 (1977).
3) H. Arnold, L. Biste, and Th. Kaufmann, *Krist. Tech.*, **13**, 929 (1978).
4) Y. Shoji, K. Tatsumi, R. Matsuzaki, and Y. Saeki, *Bull. Chem. Soc. Jpn.*, **53**, 269 (1980).
5) A. Yajima, Y. Segawa, R. Matsuzaki, and Y. Saeki, *Bull. Chem. Soc. Jpn.*, **56**, 2638 (1983).
6) H. Flaschka and H. Abdine, *Z. Anal. Chem.*, **152**, 77 (1956).
7) JCPDS, Powder Diffraction File 25-1133.
8) ASTM, Powder Diffraction File 7-7.