Formation of Aluminum Nitride Using Lithium Nitride as a Source of N^{3-} in the Molten Aluminum Chloride

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Synthesis of aluminum nitride, known as wide gap semiconductor, was attempted by the molten salt method using lithium nitride as the source of N^{3-} ion and aluminum chloride as the source of aluminum ion and the medium of lithium nitride at 250 °C. Production of aluminum nitride was recognized from the spectra of XRD and XPS. Production of aluminum nitride suggests the simple reaction mechanism that the N^{3-} ion ionized from lithium nitride in the molten aluminum chloride with Al^{3+} ion.

Synthesis of metal nitride, known as wide band-gap semiconductor, are studied actively; e.g., the chemical vapor deposition method using organometals and ammonia as reactants,[1,2] physical vapor deposition method,[3,4] direct reaction of a metal with nitrogen gas at high temperature (800-1600 °C) and the reaction with a molten metal and ammonia.[5] We attempted at synthesis of metal nitride by dissolving Li_3N into a molten $AlCl_3$ at 250°C. Reaction of Li_3N with metal cation in molten salt has been investigated by some groups.[6, 7] In the molten salt, Li_3N dissociates into $3Li^+$ and N^{3-} and dissociated N^{3-} would react with metal cation and form metal nitride. In these works, reactants, Li_3N and metal cation source, were introduced inert salts, e.g., LiCl, KCl *etc.*, and the reaction temperature was 450-1200 °C. We adopted $AlCl_3$ as a molten salt, that also participates in the reaction as the source of metal cation. In the molten $AlCl_3$, whose melting point is 190.2 °C, nitridation would proceeds at comparatively lower temperature, because this reaction is known to be very exothermic.[8]

The preparation of materials was carried out in a glove box under the atmosphere of nitrogen. Ground $AlCl_3$ (Wako Pure Chemical, 99.9%) was mixed with Li_3N (Aldrich, 99.5%) in a mortar. The molar ratio of $AlCl_3$ and Li_3N was 2:1. Mixed material was put in a ceramic boat and melted in an electric furnace under the stream of Ar. The temperature was kept at 250 °C for 5 h and then the boat was cooled gradually. Unreacted $AlCl_3$ and Li_3N were removed by washing with ethanol and the insoluble powder was filtered. The obtained powder was pressed under 200 kg cm^{-2} with a hand press into a disk of 1 cm in diameter and identified by XRD (Jeol Model JDX-85) and X-ray photoelectron spectroscopy (XPS) (Shimadzu ESCA-850). The measurement of XRD was carried out under the condition that current is 20 mA using $K\alpha$ ray of copper as the source of X-ray. The peaks of observed XRD pattern were assigned according to data of committee on powder diffusion standards (JCPDS). As the source of X-ray in the measurement of XPS, K α ray of magnesium (1.25 k eV) was used.

The XRD pattern of products is shown in Figure 1. All the peaks are assigned to that of AlN or Al and the peak of other compounds was not observed. This result indicates the reaction in the molten salt produced AlN and Al. In the spectrum of XPS, a peak of nitrogen 1s was observed around 390-410 eV. This also supports that the obtained powder contains the nitride. These results suggest that the two reactions occur in the molten salt as follows.

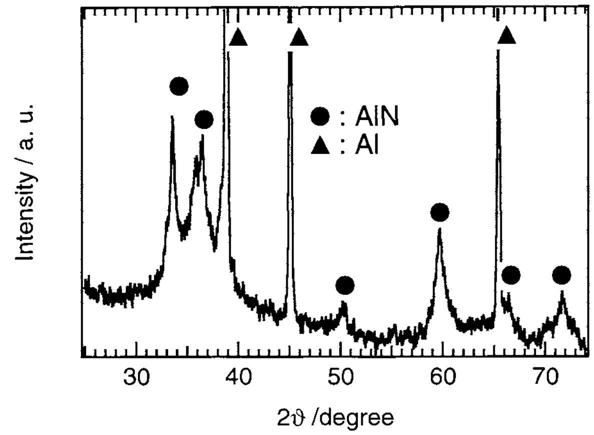

Figure 1. XRD pattern of the products of reaction in molten $AlCl_3$.

$$Li_3N + AlCl_3 \rightarrow AlN + 3LiCl \quad (1)$$
$$Li_3N + AlCl_3 \rightarrow Al + 3LiCl + 1/2N_2 \quad (2)$$

In reaction (1), Li_3N acts as the source of N^{3-}, whereas it acts as a reductant in reaction (2). In this reaction system, the source of nitrogen is only Li_3N, therefore, the production of AlN indicates the presence of N^{3-} ion in the molten salt. The ionized N^{3-} ion would react with Al^{3+} in the molten $AlCl_3$ and produce AlN as soon as Li_3N ionizes into Li^+ and N^{3-}. Production of Al indicates that Al^{3+} was reduced by N^{3-} as in reaction (2). In the molten salts, reaction (1) and reaction(2) would be competing. Changes in standard free energy of reaction (1) and (2) is -681.53 and -394.93 kcal / mol, respectively.[9] Both reactions are very exothermic. Reaction (2) also depends on the redox potential of Al^{3+} and N^{3-}. The reduction potential of Al^{3+} in the molten salts is +1.553 V vs. Li / Li^+,[10] while the oxidation of N^{3-} proceeds at +0.2 V vs. Li / Li^+ [7]; N^{3-} is very strong reductant. In ordinary case, reaction (2) should be dominant, because N^{3-} ion is very reactive. However, in this reaction system, reaction (1) is competing with reaction (2). This may be explained by the mechanism of these reactions. The process of reaction (2) would be as follows, 1. Al^{3+} and N^{3-} would produce an active complex. 2. Electrons transfer from N^{3-} to Al^{3+}. 3. Released nitrogen atoms combine and then this reaction system is stabilized thermodynamically. In the case of reaction (1), Al^{3+} and N^{3-} would be bonded and largely stabilized as soon as they form the active complex. This simplicity of reaction and large stabilization energy seem to be the reason the reaction (1) proceeds to a certain extent.

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