Synthesis of AlN particles by chemical route for thermal interface material

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Abstract

Aluminum urea chloride complex was easily synthesized by microwave irradiation from mixed solution and it was used as a precursor for further process. The complexes have proved that urea molecules constructed a coordination sphere around the aluminum atom and formed a stable structure with microwave irradiation. Molar ratio between urea and aluminum chloride was an important factor for the synthesis of AlN particles. After microwave irradiation to the solution with molar ratio (urea/Aluminum chloride) above 6, AlN particles without Al_2O_3 were formed from aluminum urea chloride by heat treatment at 1000 ℃ in nitrogen atmosphere. AlN particles with low oxygen content of 0.85 wt% were successfully synthesized at 1700 ℃ under N_2 atmosphere in the molar ratio of 6. Copyright © 2017 VBRI Press.

Keywords: AlN, urea route, microwave irradiation, nitridation.

Introduction

Aluminum nitride (AlN) has high thermal conductivity (theoretical value is 320 $Wm^{-1}K^{-1}$) [**1**], high electrical resistivity (> 10^{16} Ωm), low thermal expansion (20-500 ℃, $4.6\times10^{-1}K^{-1}$) [**2**], high stability to chemicals, and no toxicity. Due to these excellent properties, AlN have been widely used as electronic circuit components which require both high heat conductivity and good electrical insulation. These unique properties have made AlN an extremely attractive material for high-tech industrial applications such as electrical packaging and heat sinks. Therefore, much attention has been given to the preparation of AlN. In general, AlN could be fabricated by several different methods, such as carbothermal reduction and nitridation (CRN) of Al_2O_3 with carbon black in the presence of N_2 [**3-7**], direct nitridation of aluminum with N_2 or NH_3 [**8**, **9**], chemical vapor deposition (CVD) process via the $AlCl_3$-NH_3-N_2 system with various total flow rates [**10**] and plasma-based processes. Among them, CRN and direct nitridation have been the most widely used in the industrial production. However, these methods have a variety of drawbacks, such as high-energy consumption, large size products, and low pure products of direct nitridation of aluminum powders and complicated production processes, high production temperatures, long production process of CRN. Recently, a lot of researches have been done in the past few years to synthesize high purity AlN powders and reduce the fabricating cost. For example, Zhifang Gao synthesized AlN powders from urea glass route [**11**]. These researches showed that the urea/metal molar ratio could be applied to tailor molecular precursors which might play an important role in the purity and crystal structure of the formed metal nitride. The process underwent a series of reaction, such as dissolving the amount of aluminum chloride and urea into the ethanol, dehydration and then heat treatment. This reaction system offers some benefits i) easy way to synthesize precursor and its high hydrolysis resistance, ii) low nitridation temperature, iii) no deed of any additional carbon source. S. Angappan suggested that microwave-assisted synthesis to prepare the aluminum nitride [**12**]. This work showed that reactant selectivity during energy transfer from the microwave field and enhanced reaction kinetics. Microwave process compared with conventional processing favors that more uniform volumetric heating takes place and the ignition could be achieved at much lower power level. The exact nature of microwave interaction with reactants during the synthesis of materials is somewhat unclear and speculative until now. However, energy transfer from microwave to the materials is believed to occur either through resonance or relaxation, which results in rapid heating.

Above those reasons, in this report, we chose urea as ligand in order to investigate the effect of formation of complex with aluminum chloride under the microwave irradiation that induced acceleration of chemical reaction.

Urea replaces the coordinate hydroxyl group around the metal atoms, followed by heat treatment was performed in various atmosphere to reduce the oxygen contents in AlN particles. During the heat treatment, Aluminum urea chloride was decomposed, dissociated and transformed to AlN particles. The changes of chemical compositions before and after microwave irradiation were investigated by Fourier-transform infrared spectroscopy. Finally, molecular structure and chemical reaction for nitridation were suggested.

Experimental

The aluminum chloride ($AlCl_3 \cdot 6H_2O$, 97.0%), urea ($CO(NH_2)_2$, 99.0%) and anhydrous ethanol (C_2H_5OH, >99.5%) were used as raw materials to prepare AlN particles. Aluminum chloride and urea were dissolved in anhydrous ethanol to obtain a concentrated solution with metal/urea molar ratio (MR) of 1:2, 1:4, 1:6, 1:8 and 1:10, respectively. The mixture was stirred at room temperature until clear solution. Aluminum urea chloride solution was irradiated by microwave for 15 mins to change white colored aluminum urea chloride compound. Then heat treatment of this compound was performed in various gases such as N_2 (purity: 99.999%), N_2-H_2 (95%-5%) and N_2-H_2 (90%-10%) at temperatures from 1000 to 1700 °C. The flow rates were fixed at 0.5 L/min up to 800 °C and increased to 1.5 L/min above 800 °C for the efficient removal of decomposed products. The temperature at 800 °C was maintained for 4 hours and after reaching maximum temperature of heat treatments such as 1500, 1600 and 1700 °C, another 4 hours maintained to get high purity of aluminum nitride.

The composition and structure of the aluminum urea chloride complex were characterized using Fourier-transform infrared spectroscopy (FT-IR, Jasco 6300). Thermogravimetric-differential thermal analysis (TG-DTA, SETSYS Evolution 24) of the aluminum urea chloride complex was performed in N_2 atmosphere at a heating rate of 5 °C /min. The crystalline structures of synthesized AlN powders were analyzed by an X-ray diffractometer (XRD, Rigaku D/Max-2500) with CuKα radiation (λ = 1.54056 Å, 40 kV/250mA). Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F) was employed for the observation of morphology and particle size and distribution. The oxygen content of AlN powders obtained was measured by oxygen/nitrogen analyzer.

Results and discussion

Functional groups of starting materials including ethanol, $AlCl_3 \cdot 6H_2O$ and urea were analyzed using FT-IR. **Fig. 1(a)** showed typical several peaks of O-H stretch (3367 cm^{-1}), C-H stretch (2976 cm^{-1}) and C-O stretch (1089 and 1049 cm^{-1}) from ethanol. Peaks in **Fig. 1(b)** were almost the same as those of **Fig. 1(a)**, because $AlCl_3 \cdot 6H_2O$ was simply ionized without any reactions with ethanol. In **Fig. 1(c),** the stretching of N-H (3191 cm^{-1}) and C=O stretch peak (1652 cm^{-1}) appeared from urea and the others were coincident with those in ethanol. After microwave irradiation to the mixed solution, N-H bending peak (1496 cm^{-1}) and the asymmetric and symmetric NH_2 stretching peaks (3471, 3367 and 3187 cm^{-1}) were observed as shown in **Fig. 1-(d)**. On the other hand, the O-H stretch peak (3367 cm^{-1}) disappeared in **Fig. 1(d)** compared with the **Fig. 1(a), (b) and (c)**.

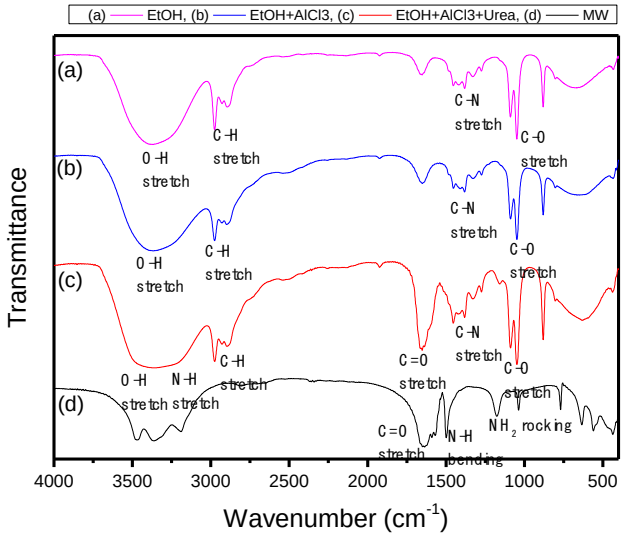

Fig. 1. Infrared spectra of (a) ethanol, (b) ethanol + $AlCl_3 \cdot 6H_2O$, (c) ethanol + $AlCl_3 \cdot 6H_2O$ + urea, and (d) ethanol + $AlCl_3 \cdot 6H_2O$ + urea after microwave irradiation.

It is probable that Urea (CON_2H_4) molecules were coordinated to the Al^{3+} via oxygen atoms and C=O double bond gained single bonding properties with the breakage of resonance structure of urea and dehydrate during the microwave irradiation as shown in **Fig. 2(a)**. Moreover, NH_2 rocking peaks (1175 cm^{-1}) were observed in **Fig. 1(d)** due to covalent bonding between urea and Al^{3+}. As a result, the disappearance of the C-H stretch peak (2976 cm^{-1}) revealed the desolvation of a matrix of ethanol. Thus, the aluminum-urea chloride was formed and its structure could be expected according to the analysis above (**Fig. 2**).

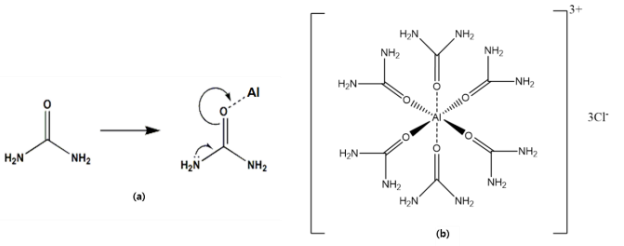

Fig. 2. Expected structure of aluminum urea chloride complex.

TG/DTA measurements were performed on aluminum urea chloride compound under nitrogen from room temperature to 1700 °C which was shown in **Fig. 3**. As can be seen in the DTA curve, three strong endothermic peaks near 180 °C, 260 °C, and 370 °C were observed. At 180 °C, an endothermic peak with slight weight loss arose. Drastic weight loss in 260 °C and 370 °C are possibly attributable to the decomposition of urea. Furthermore,

the endothermic peak accompanied a weight loss of 60 % at 370 °C. These peaks can be predicted by the following chemical reactions.

$$Al(CON_2H)_6Cl_3 \rightarrow AlCl_3 + 6CO(NH_2) \quad (1)$$

$$6CO(NH_2) \rightarrow HCNO\uparrow + NH_3\uparrow \quad (2)$$
$$\rightarrow NH_2CONHCONH_2 + NH_3\uparrow$$
$$\rightarrow C_3H_3N_3O_3 + HOCN\uparrow + 3NH_3\uparrow$$

$$CO(NH_2)_2 + HOCN \rightarrow NH_2CONHCONH_2 \quad (3)$$

$$NH_2CONHCONH_2 + HCON \rightarrow NH_2CONHCONHCONH_2 \quad (4)$$

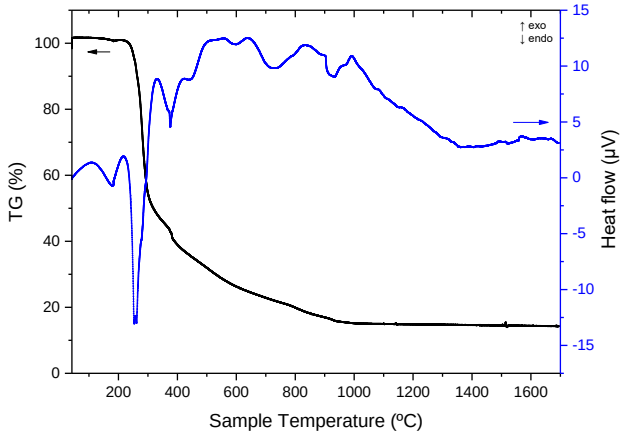

Fig. 3. TG-DTA curves of aluminum urea chloride complexes after microwave irradiation.

When the temperature exceeded 370 °C, the curve became broad because dissociation and decomposition of urea was almost completed. This revealed that aluminum urea chloride compound was synthesized with microwave irradiation, which was in agreement with the FT-IR spectra. As temperature increased to 1000 °C, the residual weight loss of the aluminum urea chloride was almost finished.

Fig. 4 showed the X-ray diffraction patterns of AlN particles synthesized from different molar ratio (MR) at 1000 °C. According to XRD patterns, a mixture of Al_2O_3 and AlN was formed in the MR 2 and MR 4 samples Results from MR 6 and MR 8 showed the identical pattern with MR10 without Al_2O_3 as an impurity. Considering the analysis of FT-IR, TG/DTA and XRD, complexation of urea with Al^{3+} in low MR was not adequate to produce enough AlN nuclei and grew independently without neighbors, and then aluminum was not coordinated by urea molecules with a stabilizing structure. A similar research was reported by Z. Gao et al. [**11**] and M. Qin et al. [**5**] found that a complete conversion to AlN required more than 1500 °C. Finally, MR 6 was chosen and heat treatment was performed at different temperatures from 1500 to 1700 °C in various atmospheres under N_2 only and N_2-H_2 mixed gas.

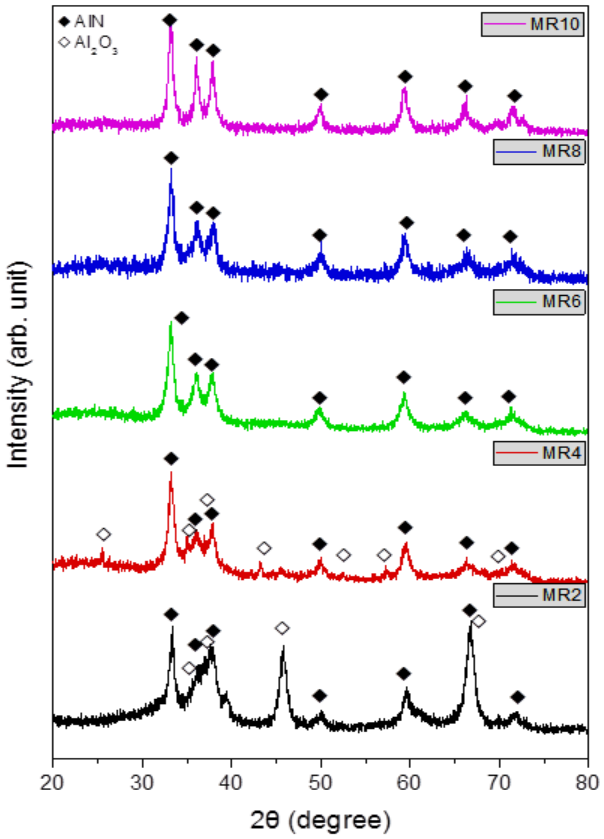

Fig. 5. XRD pattern of AlN particles after heat treatment at 1000 °C with the different molar ratio (MR).

Fig. 5 showed the XRD patterns of AlN obtained under various reaction conditions. At 1500 °C and 1600 °C, AlN phase without any impurities was found in all cases. On the other hand, a mixture of AlON and AlN was formed in mixed gas atmosphere at 1700 °C. The highest intensity of AlN patterns was obtained at 1600 °C and then the intensity of AlN peaks are increasing in

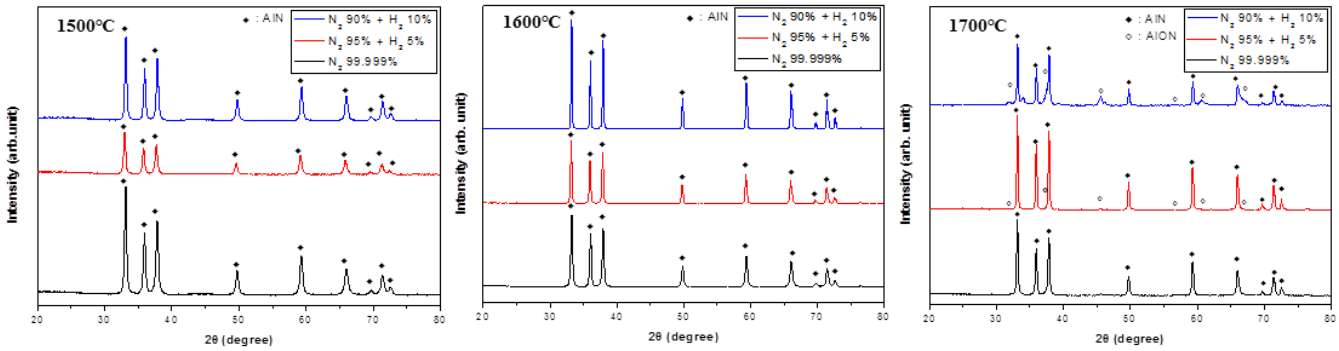

Fig. 4. XRD patterns of AlN particles under various atmospheres at different temperatures.

nitrogen gas content. Above 1700 °C, cubic AlN is an unstable and transformed into hexagonal AlN. Cubic AlN which exists with Al_2O_3 and hexagonal AlN, could be the product of AlON synthesized by Al_2O_3 and AlN **[13]**.

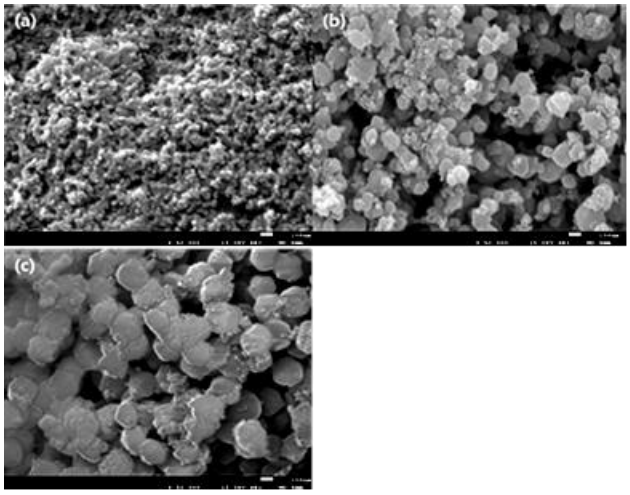

Fig. 6. FE-SEM images of AlN powder synthesized under the atmospheres of (a) N_2, (b) N_2-H_2 (95%-5%), (c) N_2-H_2 (90%-10%).

The morphology of AlN particles with various reaction conditions at 1600 °C was shown in **Fig. 6**. The particle size was in the range from 20 to 120 nm with the reaction gases and spherical in shape. As shown in **Fig. 6**, AlN particles were partially agglomerated and as H_2 content in mixed gas was increased, the particle size increased.

It means that H_2 content played an important role in the particles size and morphology of AlN particles. The oxygen contents reported in **Table 1** showed that they were increased with H_2 contents of reaction gas at 1500 °C and 1700 °C. On the contrary, the oxygen content was decreased at 1600 °C with H_2 contents of reaction gas. Conclusively high purity of AlN particles were successfully synthesized using microwave-assisted urea route followed by heat treatment for nitridation in various atmospheres based on N_2.

Table 1. Oxygen contents with reaction gas and heat treatment temperature.

Temperature (°C)	Oxygen content under N_2	Oxygen content under N_2-H_2 (95%-5%)	Oxygen content under N_2-H_2 (90%-10%)
1500	1.5403 wt %	2.4010 wt %	5.2508 wt %
1600	2.1205 wt %	2.0042 wt %	1.3001 wt %
1700	0.8492 wt %	2.4330 wt %	12.3997 wt %

Conclusion

In this study, novel route for the synthesis of AlN particles with microwave assisted method was suggested. It was found that molar ratio between urea and aluminum was an important factor for the formation of AlN phase. In order to get aluminum urea chloride powder as a precursor, microwave irradiation power and time were optimized. FT-IR results indicated that microwave induced the formation of aluminum urea chloride complex. Al ion sits on an inversion center and is surrounded by six oxygen bonded urea ligands. As the molar ratio (urea/aluminum chloride) was increased up to 6, AlN pattern was distinctly observed by XRD analyses. Finally, AlN particles with low oxygen content of 0.85 wt% were obtained by heat treatment of aluminum urea chloride complex at 1700 °C in nitrogen atmosphere for 4 hours. It is well known that thermal properties of AlN are mainly dependent on oxygen content which can decrease thermal conductivity. So, AlN particles prepared in this work could be an attractive filler ceramics for thermal interface materials.

Acknowledgements

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