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Effect of urea on synthesis of aluminum nitride powders from aluminum nitrate and glucose①

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Abstract: AlN powders were synthesized by carbothermal reduction method from aluminum nitrate and glucose. The effect of urea on the preparation and nitridation of the precursors was studied. It is found that urea can affect the morphology and composition of the precursor as well as the nitridation process. During the nitridation process of the precursor prepared without urea, α-Al_2O_3 and AlON are detected and a high temperature(1 600 ℃) is needed for a complete conversion. While for the precursor prepared with urea, a complete conversion is got at a relatively low temperature(1 400 ℃) and AlN is synthesized directly from γ-Al_2O_3, with no sign of the formation of α-Al_2O_3 and AlON. AlN powders synthesized from the precursor prepared without urea agglomerate badly, while the powders synthesized from the precursor prepared with urea are soft aggregates of fine particle, which can be easily dispersed.

Key words: aluminum nitride; urea; precursor; carbothermal reduction
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1 INTRODUCTION

Recently, aluminum nitride(AlN) has attracted much attention in advanced materials for its remarkable properties, including a high thermal conductivity ($30-260$ W·m^{-1}·K^{-1} for polycrystalline materials and 320 W·m^{-1}·K^{-1} for single crystals), a high electrical resistivity($>10^{16}$ Ω·m), a low dielectric constant(8.8 at 1 MHz) and dielectric loss($3-10$ at 1 MHz) as well as a low thermal expansion coefficient($20-500$ ℃, 4.6×10^{-6}K^{-1}) close to that of silicon. This combination of properties makes AlN an extremely attractive material for use as a substrate for high-density integrated circuits and high power electronic devices, instead of Al_2O_3 and BeO because of the low thermal conductivity of Al_2O_3 and the toxicity of BeO[1, 2]. However, the thermal conductivity and other electrical and mechanical properties of AlN ceramics are greatly affected by impurities, especially oxygen which can sharply reduce the thermal conductivity. The size and morphology of AlN powders can also affect the fabrication processes of the ceramics, such as molding and sintering. Therefore, AlN powders with a high purity and stability, small size, and sharp distribution are needed for the fabrication of high quality AlN ceramics[3].

At present, there are three main methods to prepare AlN powders: 1) direct nitridation of Al with N_2 or NH_3 [4], 2) carbothermal reduction of Al_2O_3 with carbon black in the presence of N_2 [3], and 3) chemical vapor deposition using $AlCl_3$ and NH_3 [5]. The former two methods are widely used in industry for the large-scale production of AlN powders. Compared with AlN powders made by direct nitridation of Al, the powders made by carbothermal reduction method have better properties in many aspects including the purity, sinterability and stability against humidity. However, carbothermal reduction method has also some disadvantages, such as the notorious difficulty to homogeneously mix the starting materials, the high cost based on the high calcination temperature and the demand of high purity Al_2O_3 and carbon black for the fabrication of high purity AlN powders. A lot of works have been done in the past few years to improve carbothermal reduction method, for example, Silverman[6] synthesized AlN powders from colloidal aluminum oxide precursors trapped in a polymer matrix and Hashimoto[7] prepared AlN powders from aluminum polynuclear complexes and glucose. Their researches show that the particle size and the homogeneous mixing of staring materials can greatly affect reaction conditions and properties of AlN powders. Therefore, the selection of raw materials and the preparation of a ho-

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mogeneous mixture of precursor have become the key technologies of carbothermal reduction method. In this paper, AlN powders are synthesized from water-soluble materials of aluminum nitrate and glucose, and the effect of urea on the synthesis and nitridation reaction of the precursors is studied.

2 EXPERIMENTAL

2.1 Preparation of precursors

The starting materials include: aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99% in purity), glucose ($C_6H_{12}O_6 \cdot H_2O$, 99% pure) and urea ($CO(NH_2)_2$). In our study, two precursors were prepared to investigate the effect of urea on the preparation of aluminum nitride powders. Firstly, aluminum nitrate and glucose were dissolved into 100 mL water in each of two beakers, then a certain amount of urea was added to one beaker and no urea was added to another one. The two beakers were then heated on two electrical furnaces whose temperature could be controlled. Two clear solutions were formed in the two beakers as temperature increased. In the range of 90-100 ℃, gelatinous mass was formed in both beakers with the evaporation of the solution. As heating continued, the gelatinous mass in the beaker added with urea swelled suddenly at about 120 ℃, accompanied with lots of gas released. No brown gas was observed during the whole process, which indicated that no NO_2 gas was produced. In the beaker without urea, lots of brown NO_2 gas could be observed in the reaction. Finally two precursors were prepared. The one prepared with urea was a black foamy mass and the other one prepared without urea were brown powders. These two precursors were used for the following carbothermal reduction process.

2.2 Carbothermal reduction process

The nitridation reaction of these two precursors was performed in a vertical graphite furnace. The samples were firstly held in a graphite crucible. Before heating, the furnace was vacuumed and flushed with nitrogen repeatedly, then refilled with nitrogen to eliminate oxygen before reaction. The precursor mixture was heated in a flowing nitrogen gas at various temperatures in the range of 1 200-1 600 ℃. The flow rate of nitrogen was 3 L/min. Residual carbon in each nitridation product was removed by firing in air at 600-700 ℃ for 2 h.

2.3 Characterization

Differential thermal analysis (DTA) or thermogravimetric analysis (TGA) of the solution of three raw materials was studied in air by using a thermal analyzer (Model DT-40). Phase analysis of each product calcined at different temperatures was performed on an X-ray diffractometer using Cu K_α radiation (Model 3014-Z2). The morphology and size of the AlN powders were observed using a SEM system (Model JSM-5600LU). The specific surface areas of the precursors and the products were determined by BET method.

3 RESULTS AND DISCUSSION

3.1 Effect of urea on preparation of precursors

The mixing ratio of the aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) and glucose ($C_6H_{12}O_6 \cdot H_2O$) was fixed at a $x(C)/x(Al)$ ratio of 4 (mass ratio of 1.78), and the excess of carbon source is to compensate the loss of some carbon in the preparing process. If the reactions during the preparation processes of the two precursors just include the decomposition of aluminum nitrate and urea, the $x(C)/x(Al)$ ratio may not change greatly. However, when urea was added to the solution of aluminum nitrate and glucose, the mass ratio of C to Al in the precursor obtained was 0.8, much lower than 1.78. The variation of the $x(C)/x(Al)$ ratio indicated that lots of carbon was lost in the reaction. In the precursor prepared without urea, however, the mass ratio of C to Al was 1.4, which meant that carbon loss was much less in this process. It is obvious that different reactions have taken place in the two processes.

In the solution added with urea, a large amount of heat was produced and lots of gas was released when aluminum nitrate reacted with urea. Aluminum nitrate acted as an oxidant and urea as a reductant. Some researchers[8-10] called this reaction a low-temperature combustion synthesis process. The large amount of carbon lost could be due to the combustion of some carbon source. The fact of no appearance of brown gas indicated that no NO_2 was produced. In the process of preparing precursor without urea, however, the only reaction that took place was the decomposition of aluminum nitrate. Because large amount of heat was not produced in this reaction, the loss of carbon from combustion was also little. The much less loss of carbon might be due to the evaporation of glucose during drying. Lots of NO_2 was produced when aluminum nitrate began to decompose and brown gas was seen in the reaction.

SEM images of the two precursors are given in Fig. 1 and Fig. 2 respectively. The precursor prepared without urea agglomerated badly; while the precursor prepared with urea was a foamy mass and composed of nanometric particles. The specific surface areas of the two precursors were 8.53 m^2/g and 1.27 m^2/g, respectively. The XRD analysis

Fig. 1 SEM image of precursor prepared without urea

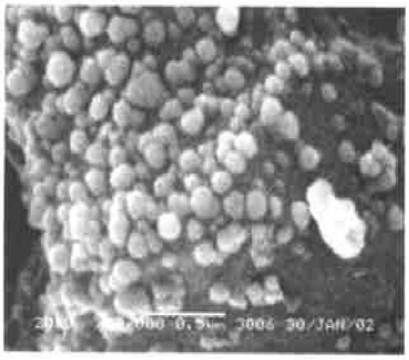

Fig. 2 SEM image of precursor prepared with urea

indicated that both of the precursors were amorphous.

3.2 Crystal phase during nitridation process

X-ray diffraction patterns of the two precursors that were calcined at different temperatures are shown in Fig. 3 and Fig. 4. For the precursor prepared without urea, α-Al$_2$O$_3$, γ-Al$_2$O$_3$ and AlON were detected in the sample calcined at 1 200 ℃, but no AlN was detected. AlN began to form and its amount increased as temperature increased. Trace α-Al$_2$O$_3$ and AlON were still detected at 1500 ℃. No other phases besides AlN could be detected when the precursor was calcined at 1600 ℃.

For the precursor prepared with urea, only γ-Al$_2$O$_3$ was detected in the sample calcined at 1 200 ℃. In the sample calcined at 1 300 ℃, a large amount of AlN was detected, while γ-Al$_2$O$_3$ diffraction peaks also remained. Single-phase of AlN was detected in the sample calcined at 1 400 ℃. During the whole nitridation process, no diffraction peaks assigned to α-Al$_2$O$_3$ and AlON were detected. It seems that in this system AlN was synthesized directly from γ-Al$_2$O$_3$ without the transition from γ-Al$_2$O$_3$ to α-Al$_2$O$_3$ and without the formation of AlON.

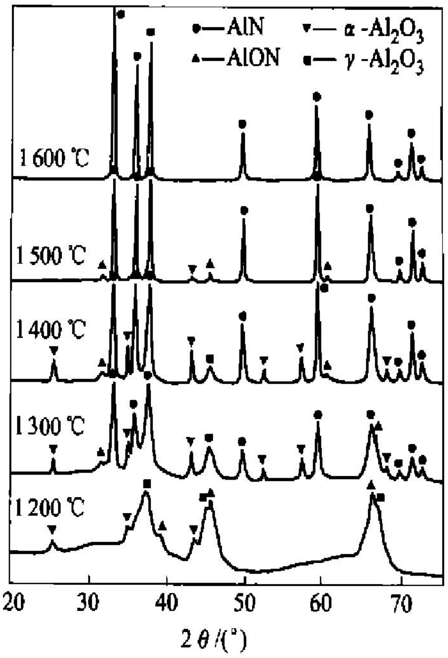

Fig. 3 XRD patterns of products from precursor prepared without urea calcined at various temperatures

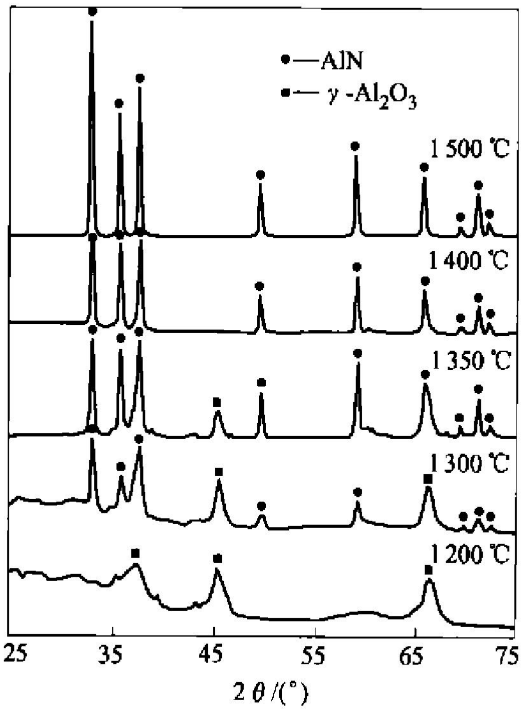

Fig. 4 XRD patterns of products from precursor prepared with urea calcined at various temperatures

It is generally known that all types of alumina would eventually transform into α-Al$_2$O$_3$ in the range of 1 100 – 1 200 ℃ in air, which is the most thermodynamically stable form of alumina at any temperature. In our experiment, however, after calcined at 1 300 ℃ for 2 h, γ-Al$_2$O$_3$ was still detected in both of the precursors and even α-Al$_2$O$_3$ was not yet detected in the precursor prepared with urea. It is evident that the phase transformation from γ-Al$_2$O$_3$ to α-Al$_2$O$_3$ was not only delayed in both of the precursors but also different in their transformation behaviors. At present, detailed reaction mechanisms of the synthesis of AlN powders by carbothermal reduction method are still unclear. Some researchers suggested that aluminum oxynitride (AlON) was formed during nitridation process and acted as an intermediate compound. In their opinion, alumina first reacted with carbon and nitrogen to form aluminum oxynitride, then aluminum oxynitride could be reduced by carbon or CO and subsequently nitrided to form AlN[11, 12]. Other researchers found that no aluminum oxynitride was formed during nitridation process and AlN powders were prepared through the direct nitridation of alumina in the presence of carbon and nitrogen[13, 14]. In our experiment, however, AlON was detected during the nitridation reaction of the precursor prepared without urea and AlON was not detected in the nitridation process of the precursor prepared with urea. It seems that the phase transformation behavior from γ-Al_2O_3 to α-Al_2O_3 and the formation of AlON during the preparation process of AlN powders by carbothermal reduction method might be related to starting materials, atmosphere, reaction rate and other factors.

3.3 Effects of urea on nitridation process

The relations between degree of conversion and calcination temperature for the two precursors are shown in Fig. 5. It can be seen that the reaction rates for the two precursors were different and nitridation reaction proceeded more rapidly in the precursor prepared with urea than that in the precursor prepared without urea.

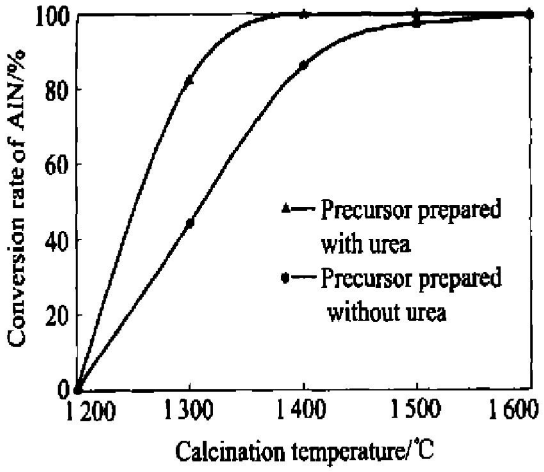

Fig. 5 AlN content vs calcination temperature

It is generally known that the reaction rate of the synthesis of AlN powders by carbothermal reduction method is closely related to the particle size and the homogeneity of the raw material mixture. In our experiment, aluminum source and carbon source could be easily mixed uniformly at molecular level after aluminum nitrate and glucose dissolved in water. During the preparation process of the two precursors, aluminum compound could be transformed into fine Al_2O_3 particles and could uniformly disperse into carbon matrix that was formed from the glucose. Therefore, in both of the precursors, the carbon and aluminum sources were homogeneously mixed. The main differences of two precursors were their powder morphology and the phase transformation behaviors during the nitridation reaction, which led to their different reaction rates.

For the precursor prepared without urea, its SEM image showed that its powders were badly agglomerated. These aggregates did not break down as temperature increased, which made it very difficult for N_2 to enter the interior of the aggregates. It seems that the inefficient supply of nitrogen hamper the nitridation reaction in this precursor. For the precursor prepared with urea, however, it was a foamy mass and had a high specific surface area, which made nitrogen could easily flow through the powders and react with aluminum and carbon sources. Therefore, the difference of nitrogen supply could cause the difference between the nitridation reaction rates of the two precursors.

The different phase transformation behaviors of these two precursors during nitridation process might be another reason for explaining their different reaction rates. It is well known that γ-Al_2O_3 has a high reactivity because of its high specific surface area. If this alumina (so called active alumina) is directly nitrided to yield AlN without the phase transformation from γ-Al_2O_3 to α-Al_2O_3, the reaction proceeds very quickly. However, the reactivity decreases rapidly when γ-Al_2O_3 eventually transforms into α-Al_2O_3. Therefore, the direct nitridation of active γ-Al_2O_3 without the formation of α-Al_2O_3 could explain the more rapid reaction rate in the precursor prepared with urea.

3.4 SEM observation of AlN powders

SEM images of the synthesized AlN powders are shown in Fig. 6. As can be seen from it, the AlN powder synthesized from the precursor prepared without urea agglomerated badly, which also indicated that the precursor did not break down during nitridation reaction. The powders synthesized from the precursor prepared with urea were soft aggregates of fine particles, which could be easily dispersed. After 2 h decarburization in air, the color of the powders obtained from the precursor prepared with urea became gray; while the color of the powders obtained from precursor prepared without urea was still black even after decarburization for 48h. The reason for this may be due to that lots of carbon had already dissolved into the lattice of AlN obtained from the precursor prepared without urea and it was very difficult to remove them.

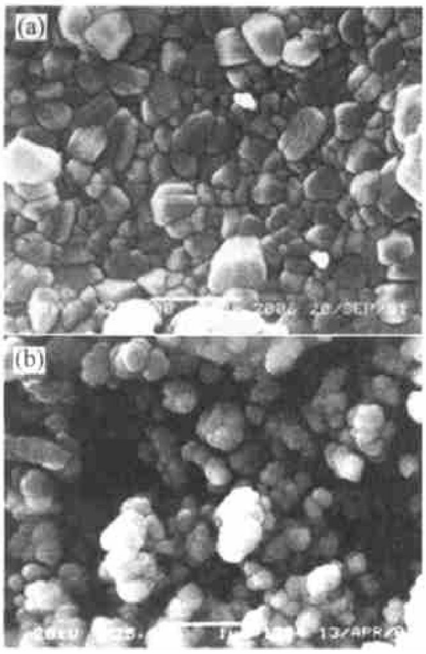

Fig. 6 SEM images of AlN powders
(a) —From precursor prepared without urea;
(b) —From precursor prepared with urea

4 CONCLUSIONS

1) Urea can affect the synthesis reaction of the precursors from aluminum nitrate and glucose, thus causes the different morphologies and compositions of the precursors obtained.

2) During the nitridation process of the precursor prepared without urea, α-Al_2O_3 and AlON are detected below 1 600 ℃ and a high temperature of 1 600 ℃ is needed for a complete conversion. For the precursor prepared with urea, however, AlN is synthesized directly from γ-Al_2O_3 without the formation of α-Al_2O_3 and AlON during whole nitridation process and a complete conversion is got at 1 400 ℃.

3) The morphologies of AlN powders synthesized from the two precursors are different. AlN powders synthesized from the precursor prepared without urea agglomerate badly; while the powders synthesized from the precursor prepared with urea are soft aggregates of fine particle, which can be easily dispersed.

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