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Effect of Ytterbia Addition on Millimeter-Wave Sintering of Aluminum Nitride†

YOSHIOKA Takashi*, MAKINO Yukio** and MIYAKE Shoji ***

Abstract

The effect of ytterbia additions on millimeter-wave sintering of aluminum nitride was examined by dependence of densification behavior and thermal conductivity. Nearly full densification was attained by the addition of ytterbia exceeding 3wt%. On the other hand, maximum thermal conductivity was obtained at the addition of 3wt% ytterbia and excess addition of ytterbia beyond 3wt% degraded the thermal conductivity of sintered aluminum nitride. From these results, it is concluded that 3wt% addition of ytterbia is the optimum condition for attaining nearly full densification and high thermal conductivity of aluminum nitride sintered at 1700°C under nitrogen with millimeter-wave heating.

KEY WORDS: (Millimeter-wave), (Sintering), (Aluminum nitride), (Densification), (Thermal conductivity)

1. Introduction

With the requirement of high integration in semiconductor devices, heat generation in the circuits becomes a serious problem for operating semiconductor devices with high reliability3). A solution for the thermal problem is to synthesize a substrate material with excellent thermal conductivity. There are various candidate materials with high thermal conductivity such as diamond and cubic boron nitride. On account of expense and difficulty of production2), however, it is difficult to use these materials as substrates commercially. Among the various candidates, aluminum nitride has attracted a considerable attention in the last decade3) on account of its excellent properties, which are high theoretical thermal conductivity (320W/(m·K))4-5) and coefficient of thermal expansion close to the value of silicon.

Hot pressing methods enable us to produce polycrystalline aluminum nitride with comparatively high thermal conductivity5). However, many problems such as the necessity of high sintering temperature and long treatment time still remain in the application of the hot pressing method as an industrial production process. Aluminum nitride can generally be densified by the addition of alkaline-earth oxides or rare-earth oxides as sintering aids6-8). The sintering aids are not only effective for achieving densification, but also for improving the thermal conductivity. Further, long annealing time under a reducing conditions at high temperature (around 1900°C) is necessary for obtaining high thermal conductivity over 200W/(m·K). Such long annealing time at high temperature is unfavorable for cost performance in industrial production, so it is desirable to develop a rapid sintering process for aluminum nitride at low temperature.

Recently, new a heating method based on millimeter-wave energy has been considered in the fields of ceramics and composites processing because rapid sintering of these materials can be performed at low temperature9-10). In our previous work, it was demonstrated that rapid sintering of silicon nitride was successfully performed at low temperature by combining millimeter-wave heating with the addition of ytterbia11). In the present study, low temperature rapid sintering of aluminum nitride with ytterbia was examined, for the purpose of verifying the excellence of ytterbia as sintering aid in millimeter-wave sintering. Millimeter-wave sintering of aluminum nitride with yttria was also performed for comparison with ytterbia-added aluminum nitride.

2. Experimental procedures

Aluminum nitride (AIN) powder (Mitsui Chemical Industry Ltd., MAN-2, average grain size 1.1 μm) was...
used as the raw material, and ytterbia (Yb₂O₃) and yttria (Y₂O₃) powder (Shin-etsu Chemical Co., RU- and UU-grades, average grain size 1.2μm and 0.25μm, respectively) were used as sintering aids. The additive content was varied from 1wt% to 6wt% for Yb₂O₃ and from 1wt% to 7wt% for Y₂O₃. Powder compacts of AlN with respective contents of Yb₂O₃ and Y₂O₃ were made by slip-casting method, after ball-milling these mixed powders for 20hr with a solvent and a dispersant. These compacts were calcined at 600°C for 1hr in nitrogen after drying. These calcined compacts were sintered in a nitrogen atmosphere of 1 atm with 28GHz millimeter-wave heating method. A high power 28GHz gyrotron generator combined with multi-mode applicator (Fuji Denpa Kogyo, FGS-10-28) was used. The heating rate was 20°C/min in the temperature range below 1500°C and 10°C/min over 1500°C. The cooling rate was fixed at 30°C/min in the range from the sintering temperature to 1400°C and thereafter the specimen was cooled in the furnace. Sintering was performed in the temperature range from 1500°C to 1850°C, and varying the holding time from 20 min. Alumina-fiber and -board were used for thermal insulation. The temperature of the specimen was measured by contacting a Mo-sheathed thermocouple of W/Re with the under side of the specimen.

Densities of the sintered aluminum nitrides were determined from the weight and volume calculated from the size. Precise densities of the sintering bodies were measured with the Archimedean method using oleic acid when the relative density was over 90%. Thermal conductivity of the sintered aluminum nitride was estimated from the specific heat and thermal diffusivity values measured with the laser flash method. These sintered specimens were coated with glassy carbon to keep the absorption of laser energy constant in the measurement of specific heat. The specimens for thermal diffusivity measurement were coated with gold to prevent laser transmission. The crystalline phases in sintered specimens were identified by XRD method using CuKα radiation.

3. Results and Discussion

In our previous paper, it was indicated that the sintering temperature of AlN with Yb₂O₃ can be lowered by using millimeter-wave heating method and nearly full densification is obtained at 1600°C. Considering the previous result, firstly, compositional dependence of densification behavior for millimeter-wave-sintered AlN was examined at 1700°C. Compositional dependence of relative density is shown in Fig. 1. Aluminum nitride with more than 98%T.D. was obtained at the content over 3wt% Yb₂O₃. On the other hand, relative density of Y₂O₃-added aluminum nitride scarcely depended on the additive content of Y₂O₃ within the composition range studied. Further, the maximum value of relative density for Y₂O₃-added aluminum nitride was somewhat lower than that for Yb₂O₃-added aluminum nitride. The slightly low sinterability of Y₂O₃-added aluminum nitride is probably attributed to lower absorbency of Y₂O₃ additive to millimeter-wave than that of Yb₂O₃ additive.

The dependence of thermal conductivity on the content of Yb₂O₃ is shown in Fig. 2. Thermal conductivity of millimeter-wave-sintered aluminum nitride increased...
rapidly in the compositional range from 1wt% to 3wt% Yb₂O₃ and the maximum value was about 180W/(m·K) for 5wt% Yb₂O₃ addition. Further, aluminum nitride with 2wt% Yb₂O₃ showed a fairly high thermal conductivity of around 170W/(m·K), irrespective of the amounts of Yb₂O₃ additive and insufficient densification. The maximum thermal conductivity was also obtained for 3wt% Y₂O₃ addition, like in the Yb₂O₃-added aluminum nitride. However, further addition of Y₂O₃ degraded the thermal conductivity of aluminum nitride. The large difference between Yb₂O₃ and Y₂O₃ additions only arises from the way of taking the unit of content in Fig. 2. When the volume percentage of sintering aid is taken as the abscissa instead of weight percentage, the maximum value of thermal conductivity is observed at about 2vol.% additive for Yb₂O₃ and Y₂O₃-added aluminum nitride, respectively.

Figure 3 shows XRD results on millimeter-wave-sintered aluminum nitrides with various Yb₂O₃ content. It was found in the figure that ytterbium garnet, Yb₃Al₅O₁₂, was the main oxide phase in all millimeter-wave-sintered aluminum nitrides. In the addition of Yb₂O₃ at less than 3wt%, ytterbium garnet phase was only observed. When the Yb₂O₃ additive exceeded 3wt%, the Yb₂O₃ appeared as another oxide phase. Especially, the peak intensity of the Yb₂O₃ phase near 2θ=30° clearly depended on the Yb₂O₃ additive content. Narrow scanned XRD patterns near 2θ=30° are given in Fig. 4. The peak of the Yb₂O₃ phase was not observed at additive contents less than 3wt% but began to appear at 4wt% Yb₂O₃. The appearance of an XRD peak due to Yb₂O₃ phase is attributed to remnant Yb₂O₃ aid that does not react with aluminum oxide in the outermost surface of aluminum nitride particles. The increase of thermal conductivity was observed until the XRD peak of Yb₂O₃ phase appeared. Similar dependence was also observed in the evolution of densification. Further, as shown in Fig. 2, thermal conductivity was degraded at the content exceeding 3wt% Yb₂O₃. Thus, the addition of 3wt% Yb₂O₃ was enough to attain full densification of aluminum nitride sintered at 1700°C in nitrogen with millimeter-wave heating and to obtain the maximum thermal conductivity of the sintered aluminum nitride.

In the Y₂O₃-added aluminum nitride, the value of thermal conductivity degraded rapidly with the increase of Y₂O₃ content, as shown in Fig. 2, and the degradation is attributed to the addition of large amount of Y₂O₃. Similar dependence was also observed between thermal conductivity and the peak intensity of Y₂O₃ phase, though not so clear as in the case of Yb₂O₃-added aluminum nitride. No XRD peak due to Y₂O₃ phase was observed at contents less than 3wt% Y₂O₃ and several peaks of Y₂O₃ phase were observed at contents more than 5wt% Y₂O₃. However, these peak intensities did not always occur regularly with the increase of Y₂O₃ content. Thus, thermal conductivity was not so clearly related to the remnant content of Y₂O₃ phase. More detailed XRD measurement is required for Y₂O₃-added aluminum nitride.

4. Summary

Compositional effects of ytterbia on densification of aluminum nitride and its thermal conductivity were examined in the millimeter-wave sintering of aluminum nitride. Addition of ytterbia more than 3wt% was
Effect of Ytterbia Addition on Millimeter-Wave Sintering of Aluminum Nitride

effective for densification of millimeter-wave-sintered aluminum nitride. Thermal conductivity of millimeter-wave-sintered aluminum nitride showed a maximum at 3wt% ytterbia and was degraded by the addition of more than 4wt% ytterbia. It was indicated that the degradation of thermal conductivity was attributed to the appearance of isolated ytterbia phases. Similar tendency was also observed in the Y₂O₃-added aluminum nitride but more detailed investigation is required to clarify the relation between thermal conductivity and the existence of Y₂O₃ single phase in the Y₂O₃-added aluminum nitride.

Reference