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Effect of primary powder in aerosol deposition of aluminum nitride

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Aerosol deposition is a very promising method to make ceramic films with several tenth of micrometer thick or more under room temperature. In the case of aluminum nitride, thick films with the thickness of several micrometers have been made. The deposition rate of as purchased primary powder was very low. The carrier gas was helium. The pre-processing of the original powder with ball milling was employed to successfully increase the deposition rate of the films. Addition of a heat treatment in the air to the milled primary powder further increased the deposition rate. The same heat treatment without ball milling as the pre-processing did not increase the deposition rate significantly. However, the primary powder of a different manufacturer showed much less increase with the ball milling pre-treatment. Some of the very small crystallites in the deposited films were transformed from wurtzite crystal structure to rock salt structure. Wurtzite structure is stable in the ambient pressure and rock salt is stable in much higher pressure environment. The crystal structure transformation was hindered by the heat treatment in the pre-processing of the primary powder. This was considered to occur by the relief of stress and strain induced during the ball milling.
Key words: Aerosol deposition, Aluminum nitride, primary powder, deposition rate, crystal structure

1. INTRODUCTION

Aerosol deposition method is a very promising method to make ceramic films with several tens of micrometer thick or more. It is a process carried out at room temperature inside a reduced pressure chamber. The method consists of dispersing primary ceramic powder in the carrier gas and blowing the produced aerosol and hence the floating primary ceramic powder particles onto the substrate accelerated by a nozzle.[1] The particles crash onto the substrate and form a solid film that adheres to the substrate firmly. No heating is necessary. Many characteristics of the aerosol deposited films are similar to those of the thin plate made by sintering. Very wide range of ceramics is successfully deposited with this method. The substrates can be metals, glasses, ceramics and plastics.

Aluminum nitride (AlN) has high thermal conductivity, thermal expansion similar to that of silicon and good dielectrical strength. Therefore it is used as electronic substrates, heat sinks and electronic packaging material. The thickness of the films successfully deposited by aerosol deposition method was less than 10 μm.[2] This thickness is insufficient for above mentioned usage, and thicker films and faster deposition rate are required of aerosol deposition of AlN.

To raise the deposition rate, pre-processing of the primary powder is said to be effective.[3] Therefore the effects of processing conditions such pre-processing of the primary powder and carrier gas flow rate are studied.

Additionally an intriguing fact was found. The crystal structure of aluminum nitride that is stable in the ambient temperature and pressure is wurtzite (hexagonal), and there are two other crystal structures that are stable in high pressure environment, rock salt (cubic) and zinc blende (cubic) structures. Even though the primary aluminum nitride powder has purely wurtzite structure as usual, most of the deposited films have both wurtzite structure and rock salt structure. This was confirmed through X-ray diffraction and transmission electron microscopy. This apparently means that the crystal structure of a part of the primary powder particles transforms from wurtzite to rock salt during the aerosol deposition. As a usual case in aerosol deposition method, the crystallite size in the deposited layer is much less than that of the primary powder crystal. This also applies to aluminum nitride and the crystallite size of the deposited films is less than 100 nm. In these small crystallites only very small crystallites with the size of less than 20 nm were found to transform from wurtzite to rock salt.[2]

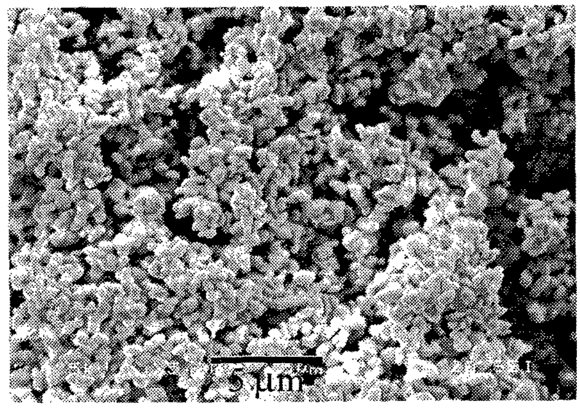
The portion of rock salt crystallite in the deposited films was found to depend on the processing conditions of aerosol deposition. The films aerosol deposited from the ball milled primary powder have taller cubic strongest peak in X-ray diffraction patterns than the hexagonal strongest peak. However when ball milled and heat treated primary powders are used, the hexagonal strongest peak is taller than cubic strongest peak.[4]

These were found in the films aerosol deposited from AlN powder made by Tokuyama Corp. There is no study made if these facts are true when a different AlN powder is used as the primary powder. Therefore the effects of powder pre-processing, gas flow rate, and the kind of primary powder are studied.

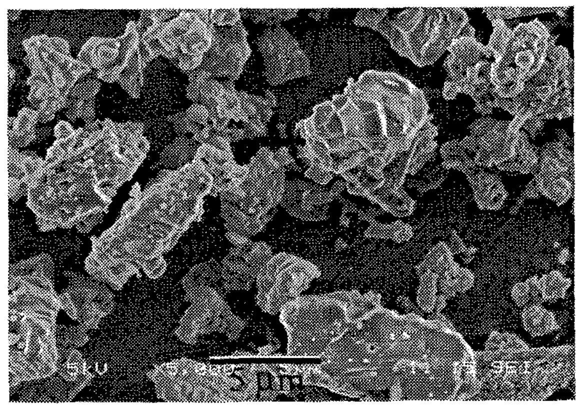
2. EXPERIMENTAL

Aerosol deposition is conducted in the machine developed in our laboratory. Helium gas was used as the carrier gas. The nozzle that accelerates the particles has 10 mm by 0.4 mm opening. The aerosol flows upwards from the nozzle. The flow rate of Helium gas is controlled by a mass flow controller and ranged from 2 l/min to 30 l/min. The vacuum pressure of the chamber varies with the flow rate of the He gas, and is the order of 100 to several thousand Pa during the deposition.

The substrate is soda-lime glass of 1.3 mm thickness, known as slide glass. It is placed under the XY stage 10 mm from the nozzle. It is moved in a reciprocating motion of 10 mm amplitude at the velocity of 1.2 mm/s. With the 10 mm nozzle opening and 10 mm displacement the resulting size of the deposited AlN film



Tokuyama AlN powder



Alfa Aesar AlN powder

Fig. 1 SEM pictures of primary powders

is around 10 mm by 10 mm.

The primary AlN powders were bought in the commercial market. One is Tokuyama AlN powder F grade, and another is Alpha Aesar Aluminum nitride powder. Tokuyama powder has nominal average powder size of 1.29 μm. Nominal size of Alpha Aesar powder is -325 mesh, which means the size is typically less than 4 μm. The SEM pictures of these powders are shown in Fig.1. Tokuyama powder is smaller in size and has smoother surface. These powders are used either as purchased, heated at 800℃ for 4h in air or pre-processed by ball milling with Fritch P-5 ball milling machine at 400 rpm for 1, 3, 5 and 7 hours with zirconia balls.

The film thickness of 2 min deposition is used as the index of deposition rate. The deposition rate for 10mm by 10mm area can be given by dividing the thickness by 2 min. However the deposition rate is not constant for long time and this value should be deemed as the early average deposition rate.

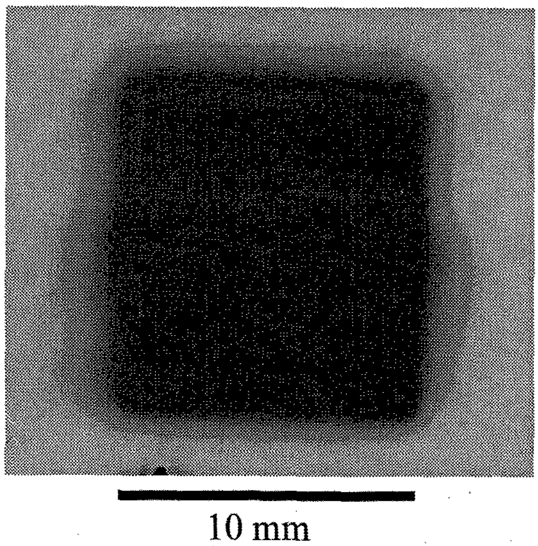


Fig. 2 Aerosol deposited AlN film, made from Alfa Aesar powder. Thickness 15μm

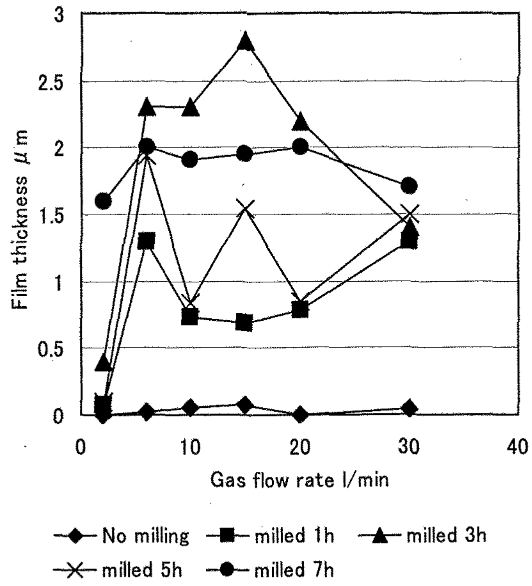
The film thickness is measured with Tokyo Seimitsu diamond stylus profilometer, Surfcom 480A. Standard Cu Kα radiation is performed with Rigaku RINT 2100V/PC diffractometer.

3 . RESULTS AND DISCUSSION

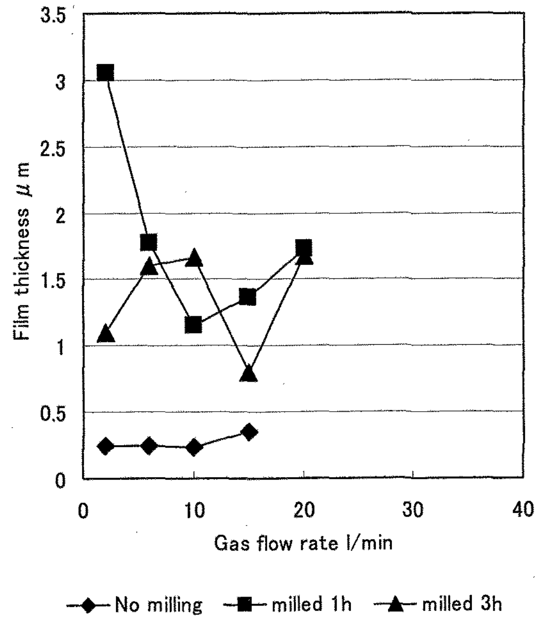
Both primary powders successfully made AlN films by aerosol deposition. Fig 2 shows one example of the films. The films of this thickness are black colored. Less thick films are gray to white.

The relationships of carrier gas flow rate, pre-processing of the primary powder and the deposition rate are investigated. Fig. 3(a) shows the relationship between the carrier gas flow rate and the film thickness of 2 min deposition for Tokuyama powder. Only very thin films are deposited at any gas flow rate with the original powder. At 2 l/min flow rate most milled powders also deposit thin films. Flow rate of 6l/min results in much thicker films. However the larger flow rates do not effectively increase the film thickness. Longer ball milling time seems to result in thicker films. compared with no milling.

Fig. 3(b) shows the relationship between the carrier gas flow rate and the film thickness of 2 min deposition for Alfa Aesar powder. With the original powder only thin films are deposited at any flow rate. However the thickness is larger than that of Tokuyama powder. Ball milling raise the deposition rate even at 2l/min flow rate.



(a) Tokuyama powder



(b) Alfa Aesar powder

Fig. 3. Thickness of the films aerosol deposited for 2 min related to carrier gas flow rate.

One hour ball milling increases the film thickness roughly 5 times. The thickness seems to be independent of gas flow rate in the experimental range.

One reason of deposition rate increase by ball milling may be the defects incurred on powder particles during

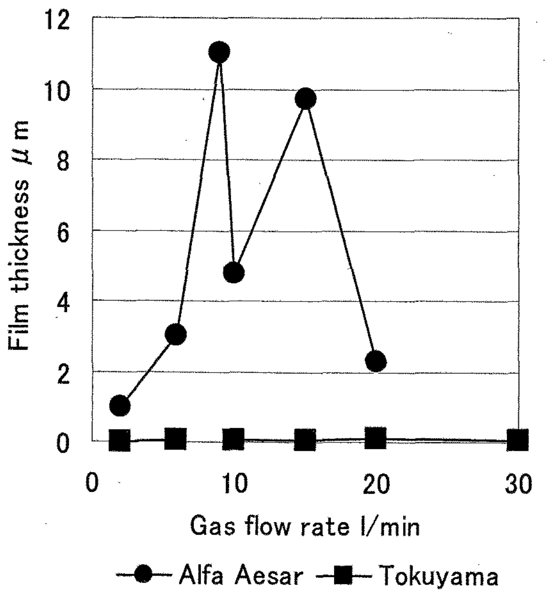


Fig. 4 Thickness of the films aerosol deposited for 2 min related to carrier gas flow rate. As pre processing, the primary powders were heated at 800℃ for 4h in air.

ball milling. Particles are broken in aerosol deposition, and the defects help the particles break at the impingement. Another reason may be the particle size adjustment. It is known from our experience that an optimal particle size range exists. However the reason is not clear yet.

The effect of heating the primary powder as pre-processing is shown in Fig. 4. The results of this treatment show big difference between the Tokuyama powder and Alfa Aesar powder. For Tokuyama powder heating has almost no effect. The film thickness is the same as non-treated powder at any gas flow rate. While Alfa Aesar powder experiences definite change and brings about very thick films. Also the thickness changes as the carrier gas flow rate increases. There seems to be an optimum flow rate. These films are much thicker than the films made by ball milled powders.

The X-ray diffraction patterns of aerosol deposited films made from two powders are measured. As the index of the portion of rock salt AlN crystallites in the aerosol deposited film, cubic to hexagonal ratio is calculated. This is the ratio of the peak heights at the strongest peak of rock salt AlN and of wurtzite AlN in a

Table 1 Cubic to hexagonal ratio of aerosol deposited films.

	milled 1h	heated
Tokuyama	1.64	1.82
Alfa Aesar	0	0.14

XRD pattern. The strongest peak of rock salt AlN lies at around 44° of 2θ value and of wurtzite AlN lies at around 33°. These results shown in Table 1 also depict the difference between Alfa Aesar powder and Tokuyama powder. Cubic to hexagonal ratios of the films made from Tokuyama powder are larger than one, which means rock salt portion is relatively larger. While the ratios of the films made from Alfa Aesar powder are far less than one, which means rock salt portion is smaller. This applies to the heated powders and to milled powders.

All those results show that characteristics of aerosol deposition of AlN are much affected by the kind of primary powders.

4. CONCLUSION

Two primary powders are aerosol deposited. Heating as pre-treatment of Alfa Aesar powder is effective in increasing the deposition rate. Ball milling as pre-treatment is equally effective to both powders. Tokuyama powder is easier to transform crystal structure from wurtzite to rock salt. The kind of primary powder is essential in aerosol deposition.

References

[1] J. Akedo and M. Lebedev, "Recent Research Developments in Materials Science, Vol. 2, Part 1", Ed. by S. G. Pandalai, Research Signpost, Trivandrum, India, (2001) 51-77.

[2] A. Iwata and J. Akedo, *Trans. MRS-J*, 29, 1097-1100 (2004).

[3] M. Lebedev and J. Akedo, *Jap. J. Appl .Phys.* 41, 3344-3347 (2002).

[4] A. Iwata and J. Akedo, *J Cryst. Growth*, in print.

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