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Phase Transformation in Aerosol Deposition Method of Aluminum Nitride

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Aerosol deposition method can form solid and semi-transparent Aluminum Nitride film on a glass or metal substrate at room temperature without any additives. The powder size used was around 500 nm. The carrier gas was He. The thickness of film successfully formed ranged from sub micrometers to 10 micrometers. The maximum thickness was limited by cracking of the film or the substrate. This indicates the adherence of the film to the substrate is very strong. Deposition rate was less than 3 μm/min for 10 mm by10 mm area. The film showed convex surface, which indicated residual stress in the film. Vickers hardness number was around 1000 which was similar to the hardness of traditionally sintered AlN. The primary powder had typical wurtzite structure, which was identified by X-ray diffraction analysis. The films showed the same peaks with a slight shift of 2θ value as the primary powder and a notable peak that corresponded to the major peak of cubic Aluminum Nitride. This indicates crystal structure transformation during the formation of the film. The relative intensity of cubic structure peak and the wurtzite structure peaks varied with processing conditions and substrate materials.
Key words: Aerosol deposition, Aluminum Nitride, film, crystal structure.

1. INTRODUCTION

Aerosol deposition is a method to make solid ceramic films at room temperature without any additives as the binders. Helium, Nitrogen, Oxygen or sometimes air is used as the carrier gas. The source pressure of the carrier gas is normally set to a little higher than the atmospheric pressure. The substrate can be glass, ceramics or metals. The method is still in research and development stage. There have been conducted several researches on oxide ceramics.[1,2] However there is few research report on other types of ceramics such as nitrides, carbides and borides. Therefore we tried aerosol deposition of Aluminum nitride (AlN). AlN is used as electronic substrates and heat sinks because of its high thermal conductivity, low thermal expansion and good dielectrical strength.

The stable crystal structure of AlN in ambient condition is wurtzite (hexagonal). Thus the AlN powder on the market has wurtzite structure. AlN also has cubic structures of Rock salt and zinc-blende. These are transformed from wurtzite at the high pressure environment such as over 14 Gpa.[3] Also they can be made as a very thin film by epitaxial growth at temperature of higher than 600°C.[4,5] A very intriguing result of this study is that cubic AlN crystals are found in the films made by aerosol deposition method even though they are made in a reduced pressure environment at ambient temperature.

2. EXPERIMENT

The aerosol deposition method is shown in Fig. 1. Note that no active heating system is included. The Helium carrier gas with the source pressure of 0.15MPa blows up the AlN powder in a mechanically shaken bottle. This generates the aerosol inside the bottle. The deposition chamber is evacuated by a mechanical booster pump and oil rotary pump combination. Therefore the aerosol is driven by the pressure difference from the bottle into the deposition chamber through the tube. The vacuum pressure of the chamber varies with the flow rate of the carrier gas, and is the order of 1000Pa during the deposition. At the end of the tube the aerosol is narrowed down by a nozzle to form an AlN particle beam with the section of 10mm by 0.4mm square and impinges on the substrate. The substrate is moved in a reciprocating motion of 10mm distance at the velocity of 1.2mm/s. Resulting size of the deposited AlN film is 10mm by 10mm.

The primary AlN powder has nominal purity of 99.8% and nominal size of -300mesh. It is made by Furuuchi Chemical Corp. This powder is used either as purchased or pre-processed by heating and/or ball milling with Fritch P-5 machine at 400rpm for some hours.

The substrates are soda glass, silica glass and molybdenum plates. The deposition time ranges from

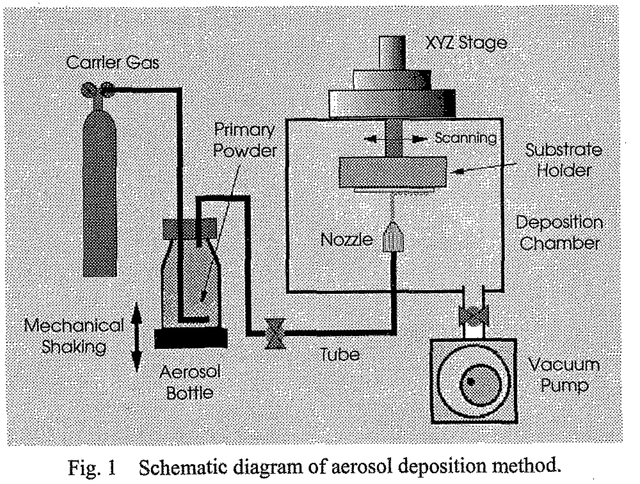


Fig. 1 Schematic diagram of aerosol deposition method.

2 to 20min.

The films are evaluated by Vickers hardness testing machine, XRD and TEM

3. RESULTS AND DISCUSSIONS

An example of the deposited film is shown in Fig. 2. This 10mm by 10mm square AlN film has the thickness of 3μm at the darker portion in the center and 1μm at the upper and lower part. It was deposited in 2min. The films and the substrates are curved in a convex manner, which suggests residual stress inside the films. The films are sometimes broken during or after the deposition when the thickness of the films is greater than 10 μm. This limits the maximum thickness of the films attained. Also the fact that the substrates are broken indicates the adherence of the film to the substrate is very strong. As shown in the figure the films are semi-transparent at the visible range.

Vickers hardness number of the films with 0.49N load lay in the range of Hv600 to Hv1200, while the hardness of the block that was sintered by hot pressing from the same primary powder was Hv1000. Hence the hardness of the films is similar to the hardness of traditionally sintered AlN.

Standard X-ray diffraction scan of the deposited AlN films using Cu Ka radiation is performed with Rigaku RINT 2100V/PC diffractometer. The diffraction patterns of the primary powder and three of the deposited AlN films are shown in Fig. 3. The primary powder has a typical pattern of wurtzite structure. The patterns of the films also have wurtzite peaks and a peak that is not found in the pattern of the primary powder at around 44 of 2θ value. This peak is identified as that of rock salt (cubic) structure of AlN.

This means that part of wurtzite structured AlN powder particles has transformed to cubic structured AlN during the deposition. The intensity of the rock salt peak relative to wurtzite peaks varies with varying deposition conditions as shown in the figure. In fig. 3(b) the Rock salt peaks are very low while in fig. 3(d) the wurtzite peaks are very low. This may mean the possibility of a new composite material that has both wurtzite and rock salt structures. Also controlling the

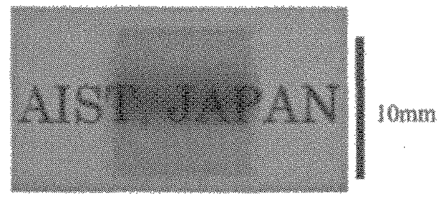


Fig. 2 Semi-transparent AlN film made by aerosol deposition with the thickness of 3μm at the darker portion in the center and 1μm at the upper and lower part.

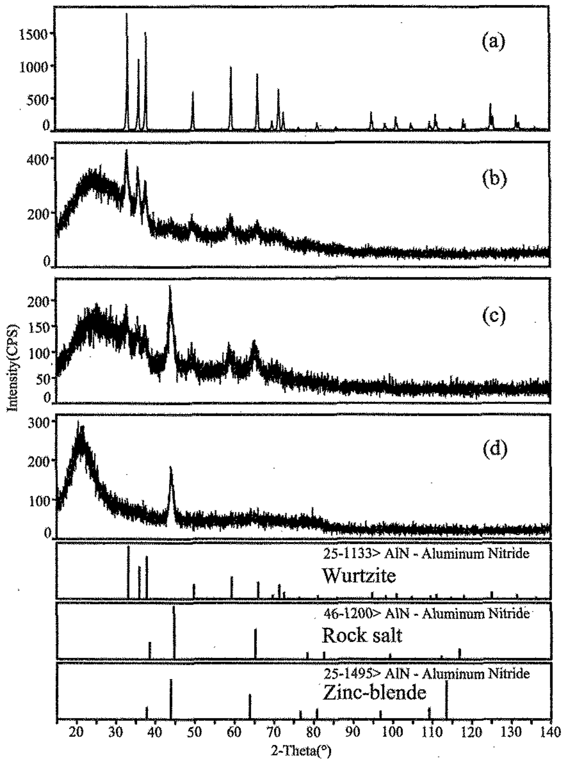


Fig.3 X-ray diffraction patterns.
(a) Primary AlN powder, (b) Milled 1h, heated 800°C, Substrate: soda glass, deposition time: 2min, (c) Milled 3h, heated 800°C, Substrate: soda glass, deposition time: 15min, (d) Heated 800°C, Substrate: silica glass, deposition time: 17min.

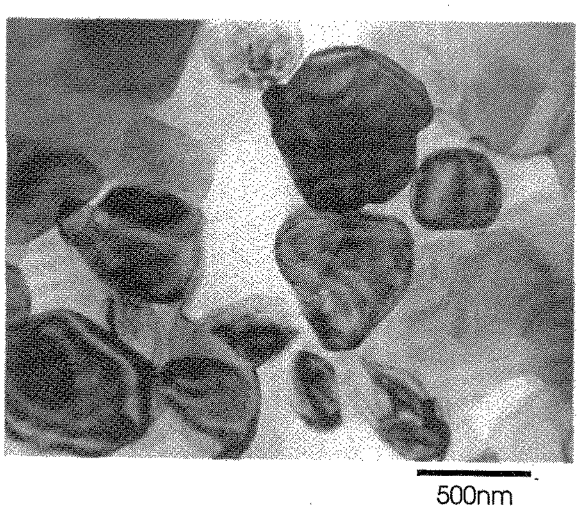


Fig. 4 TEM image of the primary AlN powder.

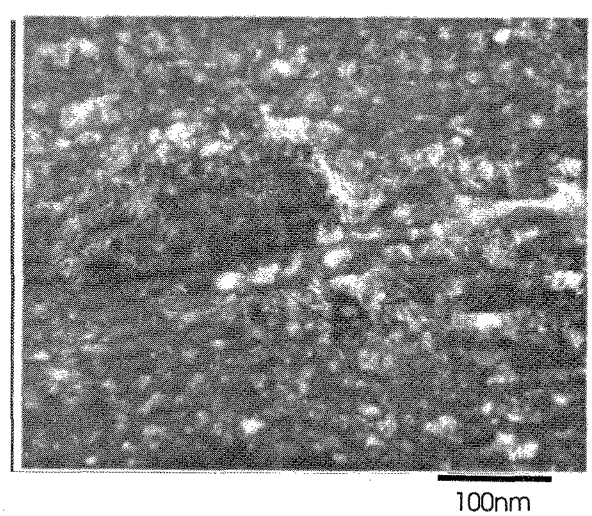


Fig. 5 TEM image of the cross section of the deposited AlN films.

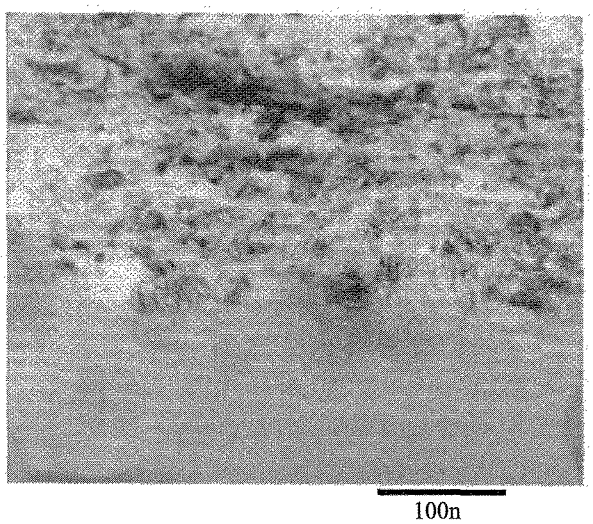


Fig. 6 TEM image of the cross section of the interface between the AlN film and the soda glass substrate.

ratio of rock salt structure in wurtzite structure may be possible.

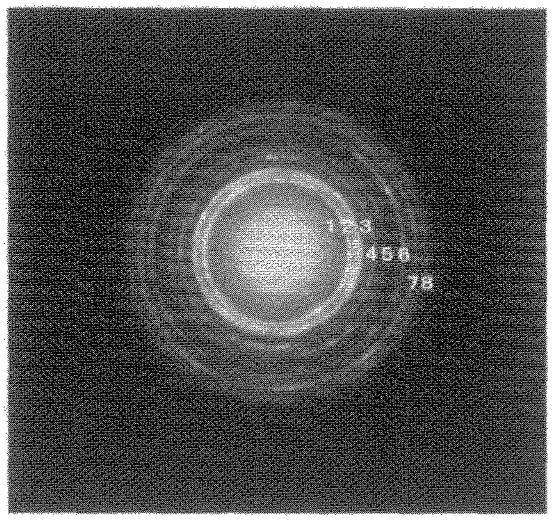
In order to confirm the existence of cubic structured AlN, transmission electron microscope (TEM) observations and electron diffraction are carried out with Hitachi H-9000UHR at 300kV. TEM image of the primary powder is shown in Fig.4. TEM images of the cross section of the deposited AlN film at the mid depth and at the bottom are shown in Fig. 5 and 6 respectively. Note the difference in the magnifications of the powder image and cross section images. The primary particles are single crystals and their major size lies around 500nm. On the other hand the film is polycrystalline and the crystal size is less than 100nm. Crystal orientations seem to be random. The interface of the film and the substrate is smooth at this magnification and wedge effect does not seem to exist.

The electron diffraction pattern shown in Fig. 7 indicates that the film consists of both wurtzite structured crystals and rock salt (cubic) structured crystals. The fourth ring that corresponds to the lattice plane distance of 0.201nm does not exist in wurtzite structured crystals and is attributed to rock salt structure of AlN.

The electron diffraction on each crystal in the film shows that bigger crystals clearly identified are all wurtzite structured. The cubic structured crystals are found in the area where crystal edges are not clear. In Fig 8 the cubic structured crystals are surrounded with black lines on the high magnification TEM image. They are smaller crystals. These crystals are found by the reverse convolution of diffraction ring of rock salt structured AlN.

These facts suggest that the primary wurtzite structured single crystal AlN particles clash onto the substrate and are broken into pieces. The smaller fragments, at least the part of them, are transformed to cubic by collision, while the bigger fragments do not experience the crystal structure transformation.

One of the factors that affect the ratio of cubic structured crystals to hexagonal structured crystals is the carrier gas flow rate. Fig. 9 shows the XRD patterns when the flow rate of Helium carrier gas was varied.



			JCPDS Card					
	measured		AlN(Wurztite)			AlN(Rock salt)		
			25-1133			46-1200		
ring No	r(mm)	d(nm)	d(nm)	Intensity	hkl	d(nm)	Intensity	hkl
1	22.0	0.272	0.269	100	100			
2	23.8	0.251	0.249	60	002			
3	25.5	0.235	0.237	80	101	0.233	30	111
4	29.5	0.201				0.202	100	200
5	34.0	0.176	0.182	25	102			
6	38.5	0.155	0.155	40	110			
7	42.0	0.142	0.141	30	103	0.143	55	220
8	45.5	0.131	0.134	5	200			

Fig. 7 Electron diffraction pattern of the cross section of the deposited AlN film shown in Fig. 5 and its analysis. The numbers in the pattern are ring numbers. The AlN film is polycrystalline and specific crystal orientation is not observed. Beside the wurtzite structure, rock salt structure is observed as the 4th ring.

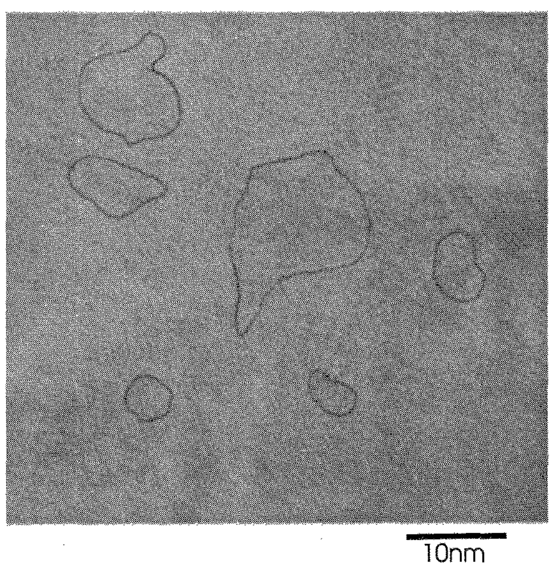


Fig. 8 High magnification TEM image of the cross section of the deposited film. The crystals surrounded by black lines have rock salt structures.

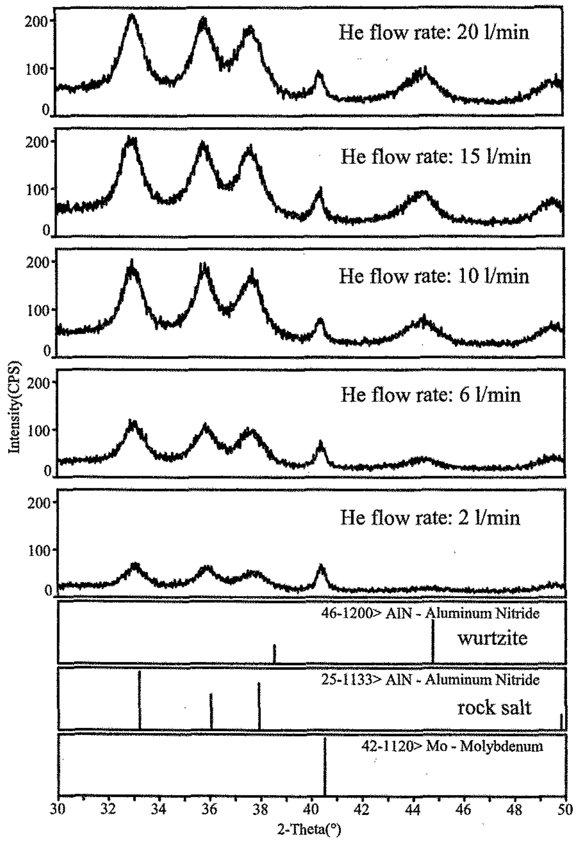


Fig.9 X-ray diffraction patterns of the AlN films made by aerosol deposition method on Molybdenum plate. The flow rate of Helium carrier gas is varied.

The substrate is Molybdenum thin plate to avoid the amorphous peak in XRD patterns. Fig. 10 is calculated from the peak intensity measurement of the strongest peaks of hexagonal AlN and of cubic AlN. The patterns appeared in fig. 9 and other XRD patterns are used. As the flow rate increases, the intensity ratio of the cubic peaks to the hexagonal peaks increases and then saturates beyond Helium flow rate of 10l/min. This suggests that the cubic/hexagonal peak intensity ratio may well depend on the degree of impact at particle impingement onto the substrate. For when the gas flow rate increases the velocity of gas increases. Consequently the velocity of the AlN particle increases and the degree of impact becomes larger.

4. CONCLUSIONS

We applied aerosol deposition method to Aluminum nitride and successfully made solid semi-transparent films of the thickness less than 10mm. The films were polycrystalline and the crystal size is less than 100nm, while the primary powder particles were single crystals with the size of around 500nm. The crystal structure of the primary powder particles were wurtzite, while the crystal structure of the films is the mixture of wurtzite structure and rock salt structure. This was confirmed with X-ray diffraction, transmission electron microscopy and electron diffraction. The ratio of these structures varied with the processing conditions, one of which is the carrier gas flow rate. This suggests the possibility of ratio control.

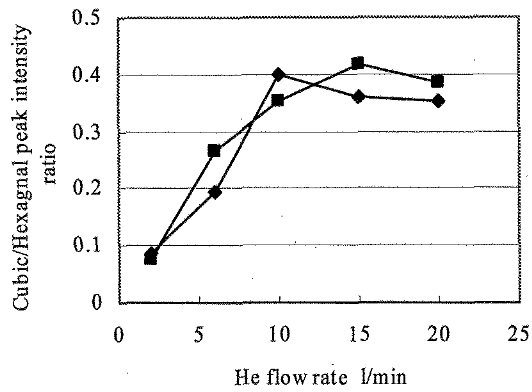


Fig. 10 Relationship between carrier gas flow rate and intensity ratio of cubic and hexagonal peaks in XRD patterns of AlN films.

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