Formation of aluminum nitride from metal–organic precursors synthesized by reacting aluminum tri-chloride with bis(trimethylsilyl)carbodiimide

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Metal–organic precursor for aluminum nitride (AlN) ceramics was synthesized by reacting aluminum tri-chloride (AlCl_3) with bis(trimethylsilyl)carbodiimide (BTSC). Fourier transform infra-red (FT-IR) spectrum of the synthesized precursor exhibited characteristic absorption bands assigned to the carbodiimide ($\text{N}=\text{C}=\text{N}$) group at 2150–2250, and 851 cm^{-1} , while the solid state ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum of the precursor exhibited single signal at 103 ppm which was thought to correspond to $\text{Al}(\text{N}=\text{C}=\text{N})_4$ unit. To examine the potential as a precursor for AlN ceramics, the intrinsic thermal conversion behavior up to 1800°C of the synthesized precursor was investigated under argon atmosphere. X-ray diffraction analysis revealed that the crystallization of AlN was found to start above 800°C , and fully crystallized AlN ceramics was synthesized by the additional heat treatment at 1800°C . In addition to the FT-IR and NMR spectroscopic analyses for studying the synthetic parameters such as reaction temperature and use of catalyst for the formation of polymeric precursors derived from AlCl_3 and BTSC, the effects of heat treatment condition on the polymer/ceramics conversion yield, impurity and crystallinity of the AlN ceramics have been studied by using a thermogravimetric analyzer coupled with a quadrupole mass spectrometer (TG-MS). The results were discussed from a viewpoint to develop a novel synthesis method for AlN ceramics through the polymer precursor route.

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1. Introduction

Aluminum nitride (AlN) ceramics have received considerable attention for their applications such as insulating substrates, heat sinks and host materials for phosphors due to their properties such as high thermal conductivity, high electrical resistivity, low thermal expansion, low dielectric constant, and wide band-gap.^{1)–19)} There are two crystalline structures in AlN, hexagonal wurzite and cubic zincblende. The wurzite structure is stable, while the zincblende structure is metastable.²⁰⁾ At present, AlN powders are produced via direct nitridation of aluminum metal, carbothermal reduction (CR) and gas-reduction nitridation (GRN) of alumina (Al_2O_3).^{21)–27)} Direct nitridation usually requires intermediate grinding between successive heat treatments to ensure complete conversion, which allows the possibility of introducing impurities. Reaction times are on the order of hours. In the CR of Al_2O_3 , controlled oxidation is required to remove unreacted carbon following the reduction, and then vacuum heating must follow, to remove any oxygen. The starting materials are more expensive than those for direct nitridation.⁷⁾ Moreover, the AlN synthesized by the GRN of Al_2O_3 exhibits high oxygen content which affecting the material properties.²⁷⁾ In this study for AlN synthesis, we have focused on the metal–organic precursor/ceramics conversion route which having potential advantages

compared with the conventional powder synthesis methods: lower processing temperatures in the synthesis of non-oxide covalent ceramics, control of the purity and compositional homogeneity in the final ceramics.²⁸⁾ In the previous studies for AlN synthesis through the metal–organic precursor route, the product prepared by reacting Me_3Al ($\text{Me}=\text{CH}_3$) with ammonia was converted into AlN upon pyrolysis.²⁹⁾ AlN was also obtained by pyrolysis of polymeric iminoalane derivatives such as $(\text{HAINH})_n$, $(\text{RAINH})_n$, and $(\text{HAINR})_n$ ($\text{R}=\text{Me}$, etc.).²⁹⁾ Additionally, the pyrolysis of the residue synthesized from aluminum tri-chloride (AlCl_3) and hexamethyldisilazane [HMDS, $\text{HN}(\text{SiMe}_3)_2$] gave AlN crystallites under Ar or NH_3 atmosphere.³⁰⁾ The detailed reaction scheme is as follows: A reaction between AlCl_3 and HMDS occurred at 60°C to form $1/2[\text{Cl}_2\text{AlNHSiMe}_3]_2$ with the simultaneous loss of one mole of Me_3SiCl . Thermolysis at 200°C of the reaction product led to forming polymeric $(\text{ClAlNH})_n$. Further pyrolysis of the polymer gave AlN crystallites ($T \geq 500^\circ\text{C}$). Furthermore, it is reported that the reaction of AlCl_3 with bis(trimethylsilyl)-carbodiimide (BTSC) yielded $\text{Cl}_2\text{AlNCNSiMe}_3$ [Eq. (1)]³¹⁾ and $\text{Cl}_2\text{AlNCNAI}(\text{Cl})\text{NCNSiMe}_3$ [Eq. (2)].³²⁾

However, a subsequent reaction of these reactants i.e., further polymerization, cross-linking and conversion into AlN ceramics

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have not studied yet. In particular, the products derived from AlCl_3 and BTSC can be expected to show a polymerization in analogy to the previously reported synthesis of silicon carbodiimide polymers by the reaction of tetrachlorosilane (SiCl_4) and BTSC with a catalytic amount of pyridine [Eq. (3)].^{33,34}

If the reaction of AlCl_3 and BTSC can be controlled to yield analogous polymeric product like $[\text{Al}(\text{N}=\text{C}=\text{N})_{1.5}]_n$, the resulting polymer will be useful as a novel meta-organic precursor for AlN ceramics. In this study, the chemical synthesis of metal-organic precursors for AlN ceramics by reacting AlCl_3 with BTSC, and thermal conversion of the synthesized precursors into AlN ceramics are investigated.

2. Experimental procedure

2.1 Precursor synthesis

All experiments were performed under pure and dried Ar atmosphere using Schlenk and glove box techniques. AlN precursor was synthesized by reacting AlCl_3 with BTSC according to the stoichiometry calculated by the following ideal reaction.

BTSC was prepared from dicyandiamide (99%, Kishida Chemical Co., Ltd., Osaka, Japan) and hexamethyldisilazane (96%, Tokyo chemical Industry Co., Ltd., Tokyo, Japan) with ammonium sulfate (99.5%, Kishida Chemical Co., Ltd.) as a catalyst according to the literature procedure.³⁵

The BTSC (7.0 ml, 0.03 mol) was added dropwise to a stirred 2.7 g (0.02 mol) of AlCl_3 (99.99%, Sigma-Aldrich Japan, Tokyo, Japan) in a 300 mL Schlenk flask. The reaction mixture was stirred at room temperature for 1 h. Then, under vacuum at 60°C, the liquid byproduct (Me_3SiCl) was distilled off, and the reaction product was isolated as highly viscous transparent liquid.

To enhance the polymerization of the reaction product, the effect of pyridine catalyst was studied. A catalytic amount of pyridine [0.89 ml (0.011 mol), 99.5%, Wako Pure Chemical Industries, Ltd., Osaka, Japan] was added to the reaction mixture, then, the mixture was stirred at room temperature for 1 h. After the distillation of the byproduct of Me_3SiCl and pyridine under the same manner mentioned above, the reaction product was obtained as white solid.

The reaction catalyzed by pyridine was also performed at 145°C by refluxing xylene used as a reaction solvent. All the chemicals mentioned above were dissolved into 5.5 ml of anhydrous xylene (Wako Pure Chemical Industries, Ltd.) at room temperature, then maintained at 145°C for 1 h. After the removal of Me_3SiCl , pyridine and xylene, the reaction product was obtained as white solid.

2.2 Pyrolysis

The synthesized precursors were pyrolyzed in a quartz tube furnace (ARF60-150-31KC, Asahi Rika Seisakusho Co., Ltd., Chiba, Japan) at temperatures of 200, 400, 600, 800, 1000°C under flowing Ar. All the samples were heated at a rate of 300°C/h to the desired temperature, held at temperature for 1 h, cooled to room temperature at the same heating rate.

2.3 Additional heat treatment

The 800°C- and 1000°C-pyrolyzed samples were ground to a fine powder using an agate mortar and pestle in a glove box. The

powdered samples were heat-treated in a graphite resistance-heated furnace (High Multi 5000, Fujidenpa kogyo, Osaka, Japan) under vacuum from room temperature to 1400°C. Then, Ar gas was introduced into the furnace at 1400°C and the temperature was increased to 1800°C with 1 h holding time under Ar atmosphere. The heating rate was 600°C/h. After the heat treatment, the samples were cooled down to room temperature in a furnace.

2.4 Characterization

Fourier transform infra-red (FT-IR) spectra were recorded using Attenuated Total Reflection (ATR) on a FT/IR-4200IF (JASCO Corporation, Tokyo, Japan) with a spectral resolution of 4.0 cm^{-1} .

Solid state ^{27}Al solid-state magic angle spinning (MAS) NMR spectra were measured on Varian UNITY Inova 400 plus (Varian, Palo Alto, California, USA), operating at 60 kHz for Al. The preparation of the samples was done under Ar atmosphere in order to avoid the hydrolysis reaction.

The thermal behavior of the synthesized precursors up to 1400°C was studied by means of TGA/MS with a simultaneous thermal analysis device coupled with a quadrupole mass spectrometer (STA 449 Jupiter®, Netzsch Japan, Kanagawa, Japan). The measurements were performed under flowing helium with a heating rate of 20°C/min.

To investigate the effect of precursor synthesis temperature on the ceramic yield, the weight loss during pyrolysis under Ar atmosphere was measured by using a conventional thermogravimetric analyzer (TG 8120, Rigaku Corporation, Tokyo, Japan) at a heating rate of 5°C/min.

X-ray diffraction (XRD) measurements of the pyrolyzed samples were performed at room temperature using $\text{Cu K}\alpha$ radiation (X'pert Pro $\alpha 1$, Philips, Amsterdam, The Netherlands). The samples were placed in holders filled with Ar in order to avoid contact with air. XRD analyses of the final product, 1800°C-heat treated samples were conducted by using a conventional sample holder ($\text{Cu K}\alpha$ radiation, X'pert, Philips, Amsterdam, The Netherlands) at room temperature.

Elemental analyses were performed on 1000°C-pyrolyzed and 1800°C-heat treated samples for silicon and aluminum (inductively coupled plasma atomic emission spectroscopy), oxygen and nitrogen (inert-gas fusion method, Model EMGA-930, HORIBA, Ltd., Kyoto, Japan), and carbon (non dispersive infrared method). The chlorine content of the 1000°C-pyrolyzed sample was determined by the ion chromatography method.

Microstructure of the 1800°C-heat treated samples was observed by using a scanning electron microscope (SEM, JSM-6360LVS, JEOL Ltd., Tokyo, Japan).

3. Results and discussion

3.1 Synthesis of metal-organic precursors and their conversion into AlN ceramics up to 1000°C

The reaction of AlCl_3 with BTSC at room temperature gave a viscous liquid product. As shown in **Fig. 1(a)**, the product exhibited IR absorption bands at 2150–2250, 1260 and 851 cm^{-1} assigned to $\nu(\text{N}=\text{C}=\text{N})$, $\nu(\text{Si}-\text{CH}_3)$ and $\delta(\text{N}=\text{C}=\text{N})$ of $\text{Si}-\text{N}=\text{C}=\text{N}$, respectively.^{33,34} Another absorption band at 808 cm^{-1} was thought to correspond to $\delta(\text{N}=\text{C}=\text{N})$ vibration of $\text{Al}-\text{N}=\text{C}=\text{N}$ bonds.

In this study, to examine the potential as a precursor for AlN, the intrinsic thermal decomposition behavior of the synthesized precursor was investigated under Ar atmosphere. **Figure 2** shows the thermal behavior of the precursor during pyrolysis up to

Fig. 1. FT-IR spectra of precursors synthesized by reaction of AlCl_3 with BTSC (a) at room temperature and (b) at room temperature in the presence of a catalytic amount of pyridine.

Fig. 2. (a) FT-IR spectra and (b) XRD patterns of precursor synthesized at room temperature and after pyrolysis at temperatures 200 to 1000°C under Ar (The diffraction peaks marked by * were originated from the special sample holder used to avoid contacting with air).

1000°C. With increasing the pyrolysis temperature, the IR absorption band due to the carbodiimide group at 2150–2250 cm^{-1} continuously decreased in intensity, and disappeared after pyrolysis at 1000°C. The absorption bands due to the Si-CH₃ (1260 cm^{-1}) and Si-N=C=N (851 cm^{-1}) disappeared above 600°C. On the other hand, the absorption band at 808 cm^{-1} tuned to be broader and shifted towards lower wavenumber. After pyrolysis at 1000°C, the sample exhibited one broad band at 716 cm^{-1} attributed to amorphous or highly distorted AlN (TO phonon mode)^{36),37)} [Fig. 2(a)].

The XRD patterns of the as-synthesized precursor, and the pyrolyzed samples are shown in Fig. 2(b). The broad diffraction peak at around 2θ (degrees) of 20, and the minor peak at 2θ (degrees) of 43 (marked by *) were originated from the special

sample holder used to avoid contacting with air. The pyrolyzed sample was X-ray amorphous up to 800°C, then the initial crystallization was found to start above 800°C, and the 1000°C-pyrolyzed sample exhibited several diffraction peaks which were identical to those of hexagonal AlN (JCPDS Card No. 025-1133).

The results of FT-IR and XRD analyses reveal that the reaction of AlCl_3 with BTSC investigated in this study could follow the previously reported scheme:^{31),32)} formation of a dimeric compound $\text{Cl}_2\text{AlNCNSiMe}_3$ by the simultaneous loss of one mole of Me_3SiCl according the Eq. (1), followed by yielding $\text{Cl}_2\text{AlNCNAl(Cl)NCNSiMe}_3$ with the elimination of second mole of Me_3SiCl as shown in the Eq. (2).

During pyrolysis to 1000°C, further condensation proceeded with elimination of the $\text{Me}_3\text{Si-N=C=N}$ end groups, which

Fig. 3. (a) XRD patterns and (b) FT-IR spectra of 1000°C-pyrolyzed samples showing enhancement of AlN crystallization by use of pyridine catalyst in the chemical synthesis of precursors.

seemed to form the ideal polycarbodiimide derivative, $[\text{Al}(\text{N}=\text{C}=\text{N})_{1.5}]_n$ as shown in the Eq. (4). However, the ceramic yield up to 1000°C was below 10%. Then, to increase the yield by enhancing the further condensation reaction during the chemical synthesis of the metal-organic precursor, the reaction of AlCl_3 with BTSC was conducted in the presence of a catalytic amount of pyridine.^{33,34)} After the reaction for 1 h, the reaction mixture was maintained under vacuum at 60°C, and the by-product of Me_3SiCl and the pyridine were distilled off. Then, the reaction product was isolated as white solid.

Compared with Fig. 1(a), in the IR spectrum of the solid product [Fig. 1(b)], the absorption band due to the $\text{Si}-\text{CH}_3$ (1260 cm^{-1}) almost disappeared. The band intensity of the $\text{Si}-\text{N}=\text{C}=\text{N}$ (851 cm^{-1}) apparently decreased, while the absorption band at 808 cm^{-1} showed remarkable increase in intensity, and slightly shifted to 791 cm^{-1} .

Figure 3 shows (a) XRD patterns and (b) FT-IR spectra of the 1000°C-pyrolyzed samples derived from the metal-organic precursors synthesized with and without pyridine catalyst. For the XRD measurements, a normal sample holder was used to examine the degree of crystallization. The peak intensity of the XRD pattern identified as AlN phase apparently increased by the use of pyridine catalyst [Fig. 3(a)]. In addition, the IR absorption band originally located at 716 cm^{-1} exhibited apparent increase in intensity and shifted to be located at 670 cm^{-1} , closely to that at 667 cm^{-1} assigned to crystalline AlN (TO phonon mode).^{36,37)}

To investigate the formation of AlN in more details, thermal decomposition behavior of the metal-organic precursor synthesized using pyridine catalyst was in-situ analyzed by using the STA technique. The results are shown in **Fig. 4**. The sample exhibited main weight loss of approximately 70% in the temperature range from 100 to 400°C, and continuous weight loss of 13% up to 1100°C [Fig. 4(A)]. The gaseous products of C_2N_2 and N_2 were detected in the two temperature ranges, 100 to 400°C and 800 to 1100°C, while Me_3SiCl was detected in the first temperature range of 100 to 400°C. Another silicon containing product, MeSiH_3 was also detected mainly at 100 to 400°C, then continuously detected up to 1100°C. Other gaseous products identified were a trace amount of residual pyridine (not shown), and HCl detected in the two temperature ranges, 100 to 400°C and 600 to 1100°C [Fig. 4(B)].

Figure 5 presents a solid state ^{27}Al MAS NMR spectrum of the 1000°C-pyrolyzed sample derived from the metal-organic

Fig. 4. (A) Thermogravimetric analysis of AlN precursor synthesized using pyridine catalyst, as well as (B) the monitoring of the pyrolysis under helium by mass spectrometry of the gaseous C_2N_2 , N_2 , Me_3SiCl , MeSiH_3 and HCl from the polymeric precursor synthesized using pyridine catalyst.

precursor synthesized using pyridine catalyst, and those of as-synthesized precursor, reagent grade of commercial AlN and starting compound of AlCl_3 . The as-synthesized precursor exhibits single signal at 103 ppm which apparently sifted towards lower field from that of AlCl_3 (-0.73 ppm). Taking into account of the results obtained by the FT-IR analysis, this signal was thought to attribute to tetrahedral $\text{Al}(\text{N}=\text{C}=\text{N})_4$ [$-\text{N}=\text{C}=\text{N} \rightarrow \text{Al}(\text{N}=\text{C}=\text{N})_3$] unit. After pyrolysis at 1000°C, the signal was further sifted to 113 ppm, and well consistent with that of AlN assigned to tetrahedral [$=\text{N} \rightarrow \text{Al}(\text{N})_3$] (AlN_4) unit.^{38,39)}

Table 1 summarizes the result of elemental analysis performed on the 1000°C-pyrolyzed sample derived from the polymeric

precursor synthesized using pyridine catalyst, and the literature data reported for the 1000°C- and 1300°C-pyrolyzed samples derived from AlCl_3 and HMDS.³⁰⁾ Both Cl and Si impurities in this study were much lower than those of the literature data, however, the resulting ceramic yield was 20%. This value was much lower than the theoretical one (47%) calculated according to the following ideal reaction.

Moreover, the 1000°C-pyrolyzed sample in this study contained relatively higher amount of oxygen (5.94 wt %) and carbon (12.2 wt %). The 1000°C-pyrolyzed sample was thought to be highly reactive towards ambient moisture, and most of the measured oxygen could be accumulated during the sample loading and transfer steps in the analysis. On the other hand, the relatively higher amount of carbon revealed that the thermal decomposition of $\text{N}=\text{C}=\text{N}$ groups yielded considerable amount of free carbon together with gaseous C_2N_2 and N_2 . Furthermore, the sum of the composition calculated for the 1000°C-pyrolyzed sample was 92.58%, which suggesting approximately 7% of unknown residue.

The proposed polymeric structure of the metal–organic precursor, and the precursor/AlN ceramics conversion behavior investigated in this study are depicted in Fig. 6. The reaction of AlCl_3 with BTSC was successfully catalyzed by pyridine to yield polymeric product composed of tetrahedral

Fig. 5. Solid state ^{27}Al MAS NMR spectra of 1000°C-pyrolyzed sample, AlN precursor synthesized using pyridine catalyst, reagent grade of commercial AlN and starting compound of AlCl_3 .

$[\text{N}=\text{C}=\text{N} \rightarrow \text{Al}(\text{N}=\text{C}=\text{N})_3]$ unit. The Me_3SiCl detected at 100 to 400°C was the by-product [shown in Eq. (4)] physically trapped within the polymeric product. However, the detection of the MeSiH_3 by the TG-MS analysis revealed the existence of the $\text{N}=\text{C}=\text{N}-\text{SiMe}_3$ end groups, and a certain amount of the unreacted BTSC which could be also physically trapped in the polymeric product. Since aluminum species were not detected, the AlCl_3 remained and the $\text{N}=\text{C}=\text{N}-\text{SiMe}_3$ end groups, and/or some of the residual BTSC could yield Me_3SiCl and unidentified compounds during the pyrolysis.

Taking into account of the results obtained by the XRD and FT-IR analyses shown in Fig. 2, decomposition of the $\text{N}=\text{C}=\text{N}$ groups to yield gaseous C_2N_2 and N_2 at 100–400°C promoted conversion of the metal–organic polymer into inorganic amorphous Al–N–C having small amount of the residual $\text{N}=\text{C}=\text{N}$ groups. At and above 800°C, the decomposition of the residual

Fig. 6. Proposed polymeric structure of the metal–organic precursor, and the precursor/AlN ceramics conversion behavior investigated in this study.

Table 1. The result of elemental analysis performed on the 1000°C-pyrolyzed sample derived from the precursor synthesized using pyridine catalyst, and the literature data reported for the 1000°C- and 1300°C-pyrolyzed samples derived from AlCl_3 and HMDS³⁰⁾

Heat Treatment Temp. (°C) in Ar	Holding Time (h)	Composition (wt %)							Starting Material
		N	O	Cl	Al	Si	C		
This study	1000	1	22.9	5.94	2.9	48.6	0.044	12.2	*BTSC
Lit. ³⁰⁾	1000	1	26.7	6.4	14	—	—	—	+HMDS
	1300	7	28.3	7.6	≤0.1	54.3	7.4	0.10	
Aluminum carbodiimide: $\text{Al}(\text{NCN})_{1.5}$		48.3	—	—	31.0	—	—	20.7	
Aluminum nitride: AlN		34.1	—	—	65.9	—	—	—	

*BTSC: Bis(trimethylsilyl)carbodiimide, +HMDS: Hexamethyldisilazane.

Fig. 7. The mass change in the temperature range between room temperature and 1200°C under Ar of the two precursors synthesized at the different temperature in the presence of catalytic amount of pyridine.

N=C=N groups lead to the formation of amorphous Al–N network composed of tetrahedral AlN_4 unit and subsequent crystallization of AlN. During the pyrolysis up to 1000°C, the residual starting compounds decomposed to yield gaseous species which could contribute to improve the purity of AlN to some extent.

3.2 Improvement of ceramic yield, purity and crystallinity of AlN derived from synthesized precursor

Based on the results shown above, the following two additional experimental studies were performed for improving the ceramic yield, purity and crystallinity of the precursor-derived AlN: (1) Increasing the precursor synthesis temperature from room temperature to 145°C by use of xylene as a reaction solvent. As shown in Fig. 3, the use of pyridine successfully catalyzed to yield polymeric precursor at room temperature, which resulted in enhancing the AlN crystallization at 1000°C. The increased reaction temperature was thought to enhance further polymerization to form highly cross-linked three-dimensional polymer network, which was expected to improve the ceramic yield and crystallinity of the precursor-derived AlN. (2) Additional heat treatment under vacuum to 1400°C and subsequent heat treatment up to 1800°C under Ar atmosphere. In this strategy, the first pyrolysis temperature was decreased to 800°C (the onset temperature of the residual N=C=N group decomposition), which was expected to reducing amount of free carbon and improvement of the crystallinity of AlN.

Figure 7 shows the mass change in the temperature range between room temperature and 1200°C under Ar of the two precursors synthesized at the different temperature. Apparently, the weight loss of the precursor due to the decomposition of N=C=N groups in the first temperature range from 100 to 400°C was suppressed by increasing the synthesis temperature to 145°C, and the resulting ceramic yield at 1000°C was successfully improved from 20 to 35%.

The results of elemental analysis performed on the 1800°C-heat treated samples are listed in Table 2. The oxygen and carbon contents were remarkably decreased by the modified pyrolysis and additional heat treatment. The chemical synthesis of precursor at

Table 2. Chemical composition and ceramic yield of the precursor-derived AlN after the heat treatment at 1800°C for 1 h in Ar

Precursor synthesis temperature	Composition (wt %)			Ceramic yield (%)
	N	O	C	
r.t.	29.2	0.37	3.77	9
145°C	32.1	0.98	1.55	18

145°C resulted in further reduction of the free carbon content in the final ceramics (from 3.77 to 1.55 wt %). As shown in Figs. 8(a)–8(c), with decreasing the carbon content, the sample color changed from black to gray, then to grayish white. On the other hand, the morphology of the sample apparently changed by the additional heat treatment. The 1000°C-pyrolyzed sample was composed of irregular shaped particles having a size range of about 0.1 to 2 μm [Fig. 8(d)]. The 1800°C-heat treated sample derived from the precursor synthesized at room temperature showed a bimodal structure composed of fine grains about 500 nm in size and coarse grains with a diameter of about 3 μm [Fig. 8(e)]. One possible reason for the partial grain growth was thought to be due to the inhomogeneous formation of small amount of liquid phase derived from AlN and relatively higher amount of silicon and oxygen impurities compared with those in the sample derived from the 145°C-synthesized precursor. On the other hand, the 1800°C heat-treated sample derived from the precursor synthesized at 145°C exhibited a uniform and fine-grained microstructure composed of equiaxed grains having a size range of approximately 200 to 500 nm [Fig. 8(f)]. Compared with the 1000°C-pyrolyzed sample, the AlN diffraction lines of this sample remarkably increased in intensity (Fig. 9). The fully crystallized fine-grained AlN could increase stability against oxidation in air, which contributing to the suppression of the oxygen contamination in the final AlN ceramics.

4. Conclusions

Metal–organic compounds were synthesized from AlCl_3 and bis(trimethylsilyl)-carbodiimide (BTSC), and to examine the potential as precursors for AlN ceramics, the intrinsic thermal decomposition behavior of the synthesized compounds was

Fig. 8. The color and SEM image of AlN ceramics derived from the precursor synthesized using pyridine catalyst. (a), (d): 1000°C-pyrolyzed sample derived from the precursor synthesized at room temperature, (b), (e): 1800°C-heat treated sample derived from the precursor synthesized at room temperature, and (c), (f): 1800°C-heat treated sample derived from the precursor synthesized at 145°C.

Fig. 9. XRD patterns of precursor-derived AlN ceramics. (a) 1000°C-pyrolyzed sample derived from the precursor synthesized using pyridine catalyst at room temperature, and (b) 1800°C-heat treated sample derived from the precursor synthesized at 145°C using pyridine catalyst.

investigated under Ar atmosphere. The results can be summarized as follows:

- (1) FT-IR and solid state ^{27}Al MAS NMR spectroscopic analyses revealed that the reaction of AlCl_3 with BTSC occurred at room temperature. The use of pyridine as a catalyst and increasing the reaction temperature to 145°C resulted in enhancing further condensation of the reaction product to give polymeric compound ideally expressed as $[\text{Al}(\text{N}=\text{C}=\text{N})_{1.5}]_n$.
- (2) The pyrolyzed compound kept X-ray amorphous state up to 800°C , then, exhibited AlN hexagonal crystalline diffraction line after pyrolysis at 1000°C .
- (3) TG-MS analysis revealed that the decomposition of the $\text{N}=\text{C}=\text{N}$ groups at 200 to 400°C with evolution of gaseous N_2 and C_2N_2 promoted the formation of amorphous Al–N–C having a small amount of the residual $\text{N}=\text{C}=\text{N}$ groups. Further decomposition of the $\text{N}=\text{C}=\text{N}$ groups at and above 800°C could lead to the formation of amorphous Al–N and subsequent AlN crystallization.
- (4) Additional heat treatment up to 1800°C was effective to improve the purity, and crystallinity of the precursor-derived AlN ceramics
- (5) One important synthetic factor in this metal–organic precursor route is formation of uniform and highly cross-linked polymer network of $=\text{Al}-\text{N}=\text{C}=\text{N}-\text{Al}=$ linkage in the chemical synthesis of precursor, which can suppress the carbon impurity and enhance the final ceramic yield after the additional heat treatment up to 1800°C .

These results suggest that the metal–organic polymer compound investigated in this study has a potential as a novel precursor for synthesizing AlN ceramics with controlled impurity.

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