

Surface roughness improvement of alumina substrates coated using aluminum nitride sol gel

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To improve the surface roughness of alumina substrates, the AlN precursor mixtures were coated on the alumina substrates. AlN precursor mixtures were coated on Al₂O₃ substrates using a sol-gel method. The AlN precursor mixtures were prepared using urea, aluminum nitrate, sucrose and a surfactant. The effects of calcination temperature and soaking time on the phase evolution, microstructure, mechanical properties and surface roughness of the coating layer were investigated. The phase evolution, microstructure and constitution of the coating layer after calcination were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron spectroscopy for chemical analysis (ESCA). It was found that Al-N-O and Al₂O₃ phases can coexist at 1300 °C after soaking for ≤ 60 min in N₂/H₂ atmosphere. The adhesive strength of coating layer significantly increased with increasing calcination temperature. The surface roughness of Al₂O₃ substrates can be improved using AlN sol gel at 1300 °C. However, the surface roughness was obviously increased at 1500 °C.

Key words: AlN coatings, Surface roughness, Ceramic substrates.

Introduction

The rapid developments and improvements in information and telecommunication technologies and the expansion of digital industries have been based to a substantial degree on electronic components with higher precision, reliability, and integration properties, and with low noise and low power consuming characteristics [1].

Aluminum oxide provides high insulation resistance and high thermal conductivity. It is the workhorse of advanced technical ceramics and has good mechanical and electrical properties, wear resistance and corrosion resistance. It is used as an electrical insulator in a number of electrical and electronic applications, such as ceramic substrates. Alumina substrates are the most commonly used substrate in the electronics industry because of their excellent mechanical, thermal, and electrical properties compared with other oxide ceramics and because of the abundance of raw material [2-4].

Aluminum nitride is one of the most versatile group III-V compounds. It possesses a large energy band gap of approximately 6.2 eV [5], high thermal conductivity, high breakdown voltage, high electrical resistivity, low dielectric constant, and low thermal expansion coefficient. It is used as a substrate and packaging material for microelectronic devices and as a heat sink because of its heat dissipation properties [6]. Moreover, nanocrystalline

aluminum nitride (AlN) has excellent sintering properties and hence is effective in producing fully dense materials [7].

AlN powders can be synthesized mainly by two methods, one is carbothermal reduction nitridation (CRN) of alumina powders, and the other one is direct nitridation (DN) of aluminum powders. The CRN synthesizes more attractive since AlN powders produced by this method have high purity, good resistance against moisture and high sintering ability [8-10].

The sol-gel process is an important technique for producing high quality glasses and fine ceramics, and especially for synthesizing coatings. Preparing coating layers using this process, presents many advantages such as low temperature, low cost and the possibility of coating different substrate materials and complex geometries [11-13]. Low-temperature formation and fusion of the crystals are the main advances of the sol-gel process in comparison with conventional methods.

Several papers have reported studies of sol-gel coatings on alumina substrates. Touzin et al. reported that highly porous ceramic substrates were coated using a sol-gel method, and the result shows that the coatings presented good adherence to the substrate and decreased the roughness of the substrate [11]. Leivo et al. reported on ceramic coatings coated on α -alumina substrates by a sol-gel process. Their goal of their research was to establish an amorphous aluminosilicate ceramic on the Al₂O₃ substrates. However, they focused on biomaterials [14]. Lee et al. reported that the roughness of Al₂O₃ substrates could be improved by Si-Ca-Zn-O coatings produced by a sol-gel method. Meanwhile, the electrical properties of resistors were

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improved using Si-Ca-Zn-O coatings [15].

In this study, AlN precursor mixtures coating layer was prepared using a sol-gel method, and the AlN precursor mixtures was coated on a commercial Al₂O₃ substrate by spin coating. The effects of calcination temperature and soaking time on the phase evolution, microstructure, mechanical properties and surface roughness of the coating layer on Al₂O₃ substrates were investigated.

Materials and Methods

Preparation of AlN powders

The starting materials included aluminum nitrate (Al(NO₃)₃·9H₂O, 99%), urea (CO(NH₂)₂, 99%), sucrose (C₁₂H₂₂O₁₁, 99%), and a surfactant (tri-block amphoteric copolymer). First, a clear solution was prepared by dissolving a certain amount of aluminum nitrate, sucrose and urea in water. Then, the solution was heated to 95 °C on an electrical furnace, and a gelatinous mass was formed by the evaporation of the solution. Finally, a black foamy mixture of alumina and carbon (Al₂O₃ + C) was obtained. The nitridation reaction of the precursors was carried out in a vertical graphite furnace. The samples were contained in a graphite crucible. The precursor mixture was heated under flowing nitrogen gas at various temperatures in the range of 900-1500 °C for 5, 30, 60 or 120 min. The flow rate of the N₂ gas was 1 L/min. Residual carbon in each nitridation product was removed by firing in air at 700 °C for 60 min [16]. The raw materials for the synthesis of AlN powders are listed in Table 1.

Preparation of AlN precursor mixtures coating layer on Al₂O₃ substrate

The ceramic substrate was 96% Al₂O₃, and was made by Leatec Fine Ceramics Co., Ltd. From experiments on the synthesis of AlN powders, the optimum composition of the precursor mixture was applied. The coating layer on the aluminum-oxide substrates were prepared from the precursor mixture by spinning at 2000 rpm, and then heating in the plate at 200 °C until dry. The AlN precursor mixtures coating layer on the Al₂O₃ substrates were calcined in N₂-H₂ mixed gas at 900-1500 °C for 5, 30, 60, and 120 min. Afterwards, the microstructure, roughness, adhesion and thermal conductivity of the coating layer on the

Al₂O₃ substrates were analyzed.

Analysis and measurement

The phase structure was analysed by X-ray diffractometry (XRD Bruker D8 Advance) with Cu-K α radiation, a 40 kV voltage, a 40 mA current, 2 θ values between 20 ° and 80 ° at interval 0.02 °, and a 2 °/min scan speed. The microstructure and film thickness were obtained using field emission scanning electron microscopy (FE-SEM, Jeol JEL-7600F Japan). An atomic force microscope (AFM) was used for analysis of the surface roughness. The adhesion between the coating layer and the aluminum oxide substrates was analyzed by a vertical tensile tester (Shimadzu EZ Tester, Japan) with a 0.1 mm/min tensile speed. AlN powders were tested by thermogravimetric analysis (Perkin Elmer- Pyris 1 TGA) under N₂ gas and heated from room temperature to 1200 °C at a rate of 5 °C/min. The thermal conductivity of the coating layer was measured by a thermal conductivity analyser tester (Hot Disk TPS 2500).

Results and Discussion

AlN powder

The AlN powders were synthesized using aluminum nitrate, urea, sucrose and a surfactant. Fig. 1 shows the XRD patterns of AlN powders synthesized with different sucrose content and calcined at 1500 °C for 120 min. Two phases coexist at 0.25 at% sucrose: one is α -Al₂O₃, and the other is AlN. The AlN single phase with a hexagonal structure was observed when the content of sucrose was \geq 0.625 mol%. The XRD analysis indicates that a single AlN phase can be synthesized by adding more sucrose to induce the nitriding reaction. However, too much added sucrose will obstruct the grain growth of AlN.[17] It is well known that AlN powders can be synthesized by carbothermal reduction nitridation (CRN); this is a

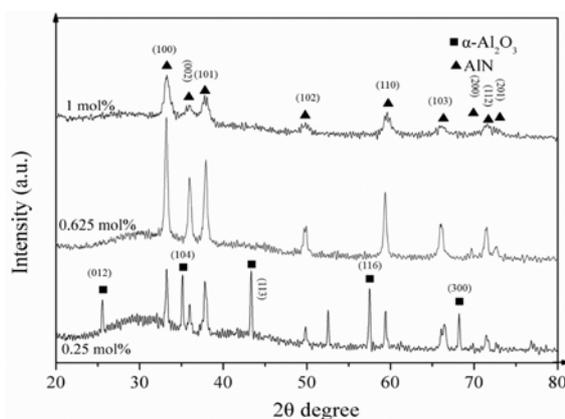


Fig. 1. X-ray diffraction patterns of the precursor mixture prepared with different sucrose content as the carbon source after calcination at 1500 °C for 120 min.

Table 1. Raw materials of the synthesized AlN powders.

Content of the additions	
D.I. water	50 ml
Aluminum nitrate	1 mol%
Surfactant	1.5 g
Urea	2.5 mol%
Sucrose	0.25, 0.625, 1 mol%

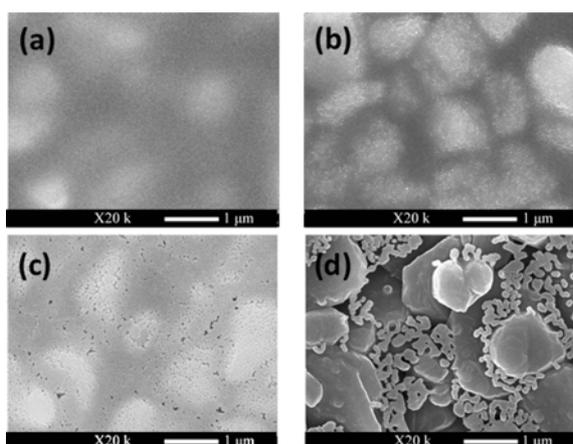


Fig. 5. SEM images of AlN coating layer on Al_2O_3 substrates calcined at different temperatures for 120 min; (a) 900 °C, (b) 1100 °C, (c) 1300 °C, (d) 1500 °C.

microscopy (TEM).

Fig. 5 shows SEM images of the precursor mixture coated on Al_2O_3 substrates calcined at different temperatures for 120 min. The AlN precursor mixtures coating layer completely cover the Al_2O_3 substrates after 900-1100 °C. When the calcination temperature reached at 1300 °C, some pin-holes were observed in the coating layer as shown in Fig. 5(c). With increasing calcination temperature, an incomplete coating layer structure was observed at 1500 °C, as shown in Fig. 5(d), where some particles remain on the Al_2O_3 substrate. Two reasons are proposed: 1) AlN precursor mixtures coating layer on the Al_2O_3 substrates is too thin (~1 nm), and strong shrinkage can occur at higher calcination temperatures. 2) oxygen atoms in the Al_2O_3 substrate can be reacted with carbon atoms of the precursor to synthesize CO_2 gas during calcination in the $\text{N}_2\text{-H}_2$ mixed atmosphere. Therefore, a lot of loss the coating layer will occur when CO_2 escapes. These observations will be proved later by ESCA and TEM analysis.

Elemental analysis of the AlN precursor mixtures coating layer on the Al_2O_3 substrates calcined at 900-1500 °C for 120 min was performed using ESCA, as shown in Table 3. The content of O in the coating layer increases with increasing calcination temperature. In contrast, the content of C decreases in the coating layer with increasing calcination temperature. In addition, N was not detected above 1300 °C. This result indicates that the $\alpha\text{-Al}_2\text{O}_3$ phases were formed easily in the coating layer at high calcination temperature. However, we think that oxygen came from the Al_2O_3 substrate, although the specimens calcined in $\text{N}_2\text{-H}_2$ atmosphere. As is known, the activation energy of $\alpha\text{-Al}_2\text{O}_3$ is 8.4 kJ/mol at 1200 °C, which is much lower than the 529 kJ/mol of AlN [18-19].

Table 4 lists the ESCA results of the AlN precursor mixtures coating layer on Al_2O_3 substrates calcined at 1300 °C for different soaking times. A little nitrogen

Table 3. ESCA of the precursors mixture on the Al_2O_3 substrates calcined at 900-1500 °C for 120 min.

Calcination temp.	Element (at%)			
	Al	O	C	N
900 °C	18.73	46.81	33.74	0.72
1100 °C	22.42	51.58	25.24	0.53
1300 °C	25.58	57.35	17.07	0
1500 °C	27.28	62.21	10.51	0

Table 4. ESCA of the precursors mixture on the Al_2O_3 substrates calcined at 1300 °C for different soaking times.

Soaking time	Element (at%)			
	Al	O	C	N
5 min	23.23	50.50	19.83	6.44
30 min	22.35	53.46	20.98	3.21
60 min	25.69	51.45	19	3.86
120 min	25.58	57.35	17.07	0

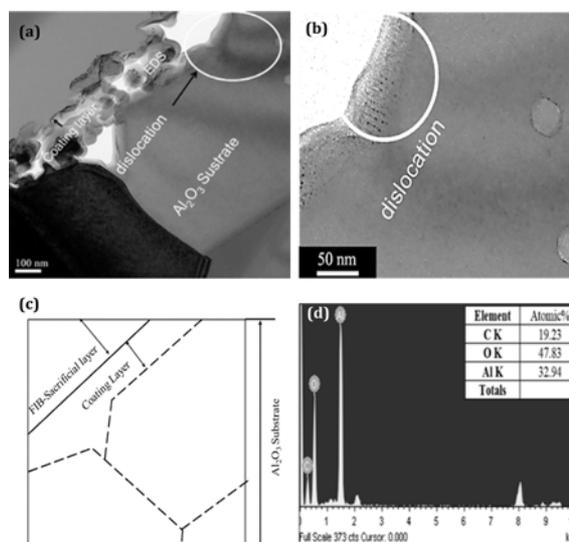


Fig. 6. TEM images of the coating layer on the Al_2O_3 substrate calcined at 1300 °C for 120 min; (a) bright field image, (b) dislocations, (c) schematic diagram of the coated precursor, and (d) EDX analysis.

can be detected in coating layer when the soaking time was reduced from 120 min to 60 min at 1300 °C. This result indicates that Al-N-O and Al_2O_3 can coexist at 1300 °C after soaking for ≤ 60 min. The stability diagram of a carbon saturated Al-N-O system at 1350 °C is well known. From the stability diagram, it can be found that AlN exists as a stable phase when the partial pressure of oxygen within the system is less than $10^{-25.5}$ atmosphere at 1350 °C for 1 atm pressure of nitrogen [18]. Therefore, it is possible that the Al_2O_3 substrate will release oxygen to react with Al atoms in the precursor mixture at high temperature under $\text{H}_2\text{-N}_2$ atmosphere.

Fig. 6 shows TEM images of the AlN precursor mixtures coating layer on the Al_2O_3 substrates calcined

Table 5. Thermal conductivity of the precursor mixture calcined at different temperatures for 120 min.

Calcination temp. (°C)	Surface roughness Ra (nm)	Adhesion force (MPa)	Thermal conductivity (W/m·K)
uncoated	82.5	-----	26.4
900	33.7	1.9	25.6
1100	44.1	7.8	25.9
1300	63.3	8.8	27.2
1500	142.4	9.2	26.1

at 1300 °C for 120 min. It can be seen that the structure of the coating layer loosens, as shown in Fig. 6(a). This result is the same as the results of the SEM analysis (Fig. 5(c)). It is interesting that some dislocations were found near the interface of the Al₂O₃ substrate, as shown in Fig. 6(b). This is evidence to prove that oxygen in the coating layer came from the Al₂O₃ substrate, as we mentioned in the above section. No nitrogen was detected by the EDX analysis, as shown in Fig. 6(d), which means that the AlN compound was not synthesized at 1300 °C for soaking time of 120 min in H₂-N₂ atmosphere. This result is consistent with the result of the ESCA analysis (Table 3).

Results from the AFM analysis (10 μm × 10 μm) of the AlN precursor mixtures coating layer on Al₂O₃ substrate calcined at different temperatures for 120 min are listed in Table 5. The surface roughness of the samples was influenced significantly by increasing the calcination temperature. There was an obvious improvement in the surface roughness at temperatures ranging from 900 °C to 1100 °C. However, it was found that the surface roughness becomes significantly worse at 1500 °C; this is attributable to the thinner coating layer accompanied by strong shrinkage, which could not completely cover the surface of the Al₂O₃ substrates at high temperature.

To examine the adhesive strength between the coating layer and the Al₂O₃ substrates, a tensile test was applied. The adhesive strength of the AlN precursor mixtures coating layer calcined at different temperatures for 120 min is also listed in Table 5. The adhesive strength markedly increased at increased calcination temperatures. The adhesive strength of the coating layer was 1.9 MPa at 900 °C, and the adhesive strength reached 7.8 MPa at 1100 °C. From the XRD analysis, we deduced that the coating layer reacted with the Al₂O₃ substrates during calcination.

The thermal conductivity of samples calcined at different temperatures for 120 min is exhibited in Table 5. With increasing of calcining temperature, there are no obvious differences in the thermal conductivity between samples. The reason for this is attributed to the Al₂O₃ phase formed in the coating layer, according to ESCA and TEM-EDX analysis.

Conclusions

1) AlN powder synthesis: Aluminium nitrate (Al(NO₃)₃·9H₂O), urea (CO(NH₂)₂), sucrose (C₁₂H₂₂O₁₁), and a surfactant (tri-block amphoteric copolymer) were used as starting materials. AlN powders can be successfully synthesized by carbothermal reduction with the addition of 0.625% sucrose and calcination at ≥ 1300 °C. The particle size of the synthesized AlN powders is very fine and below 40 nm.

2) AlN precursor mixtures as coating layer: The AlN precursor mixture with the addition of 0.625 mol% sucrose was coated on an Al₂O₃ substrate and calcined at 900-1500 °C for different soaking times. It was found that Al-N-O and Al₂O₃ phases can coexist at 1300 °C after soaking for ≤ 60 min. Some dislocations were observed near the interface of the Al₂O₃ substrate. This is evidence to prove that oxygen in the coatings came from the Al₂O₃ substrate. The adhesive strength of the coating layer significantly increased with increasing calcination temperature. The surface roughness of the coating layer was significantly influenced by increasing the calcination temperature. Especially, it was found that the surface roughness was obviously increased at 1500 °C. With increasing of calcining temperature, there are no obvious differences in the thermal conductivity between samples.

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