

Article

High-Thermal-Conductivity AlN Ceramics Prepared from Octyltrichlorosilane-Modified AlN Powder

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Abstract: Aluminum nitride has been widely used as heat-management material for large-scale integrated circuits and semiconductor packages because of its excellent insulation, high thermal conductivity, low dielectric constant and loss, similar expansion coefficient to that of silicon, and non-toxicity. However, the increase of oxygen content caused by the hydration of aluminum nitride powder during storage often decreases the thermal conductivity of aluminum nitride ceramics. In this work, we propose an approach for preparing high-thermal-conductivity AlN ceramics via octyltrichlorosilane-modified AlN powder. The octyltrichlorosilane reacted with the hydroxyl group on the surface of the AlN powder forming a siloxane protective layer. The protective layer not only enhanced the water contact angle of AlN powder from 34.8° to 151°, but also ensured the phase of AlN powder did not change in the distilled water at 25 °C for 72 h. High-thermal-conductivity AlN ceramics up to 186 W·m⁻¹·K⁻¹ were successfully prepared based on the modified AlN powder which had been stored for one year. This work provides a simple, effective, and practical method for the stable preparation of high-thermal-conductivity AlN ceramics.

Keywords: AlN ceramics; octyltrichlorosilane; surface modification; hydration resistance; AlN powder



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1. Introduction

Aluminum nitride (AlN) has been widely used as heat-management material for large-scale integrated circuits and semiconductor packages because of its excellent insulation, high thermal conductivity, low dielectric constant and loss, similar expansion coefficient to that of silicon, and non-toxicity [1–4]. However, the oxygen impurities in the AlN powder easily diffuse to the interior front of the lattice to replace the nitrogen atom and form aluminum atom vacancies, reducing the thermal conductivity of the AlN ceramics [5,6]. Hence, high-thermal-conductivity AlN ceramics can only be achieved based on AlN powder with high purity, small particle size, and narrow particle-size distribution [7]. Until now, there have been two main methods of preparing high-purity AlN powder: (1) direct nitridation of Al powder in the presence of nitrogen and (2) carbothermal reduction–nitridation of Al₂O₃ powder and carbon black under a nitrogen atmosphere. [8–11]. Generally, there has been an aluminum oxide/aluminum hydroxide layer that was several tens of nanometers thick on the surface of these AlN powders [12–14]. However, the oxygen content would increase after long-term storage because the surface layer could not effectively inhibit the hydration of AlN powder [15,16]. Therefore, improving the hydration resistance of AlN powder by surface modification is essential for the stable preparation of high-thermal-conductivity aluminum nitride ceramics.

To improve the hydration resistance of AlN powder, physical coating or chemical surface modification was usually adopted to build a protective layer on the surface of AlN powder to avoid the contact between AlN and water [17–20]. Compared to the physical coating of ceramic powder, chemical surface modification technology has been widely

adopted because of its high efficiency, fast reaction period, and controllable film-thickness. In this modification process, organic carboxylic acid, inorganic acid, coupling agents, and other surfactants that consist of hydrophobic and hydrophilic functional groups are adsorbed on the surface of AlN powder by chemical bonds to avoid AlN powder contact with water. For example, Egashira et al. [21] studied the effect of various carboxylic acids on the hydration resistance of AlN powder. Their results showed that the more carbon atoms in carboxylic acid, the better the hydration resistance of modified AlN powder, and stearic acid had the best effect on improving the hydration resistance of AlN powder. Kernel et al. [22] compared the effects of silicic acid, aluminum dihydrogen phosphate, and phosphoric acid on the hydration resistance of AlN powder. They found that AlN powder with aluminum dihydrogen phosphate as the surface modifier had the most efficient hydration resistance. Xu et al. [23] used silane coupling agent KH550 to treat the surface of aluminum nitride. They found that the pH value of the modified powder could be kept unchanged for 24 h after being heated in a 70 °C water bath. Although the above methods achieved good results in improving the hydration resistance of AlN powder, there were still some disadvantages such as complicated treatment process, low recovery rate, and high cost. Therefore, how to improve the hydration resistance of AlN powder simply, efficiently, and economically is still a bottleneck that restricts the stable preparation of high-thermal-conductivity AlN ceramics.

To solve the above problem, a facile and efficient strategy was successfully proposed to prepare high-thermal-conductivity AlN ceramics using octyltrichlorosilane-grafted AlN powder. The octyltrichlorosilane reacted with the hydroxyl group on the surface of the AlN powder forming a siloxane protective layer. The siloxane protective layer not only increased the water contact angle of the AlN powder from 34.8° to 151° but also ensured that the phase of the AlN powder did not change in a 25 °C water bath for 72 h. High-thermal-conductivity AlN ceramics up to 186 W·m⁻¹·K⁻¹ were prepared based on the modified AlN powder which had been stored for one year. This work provides a simple, effective, and practical method for the stable preparation of AlN ceramics with high thermal conductivity.

2. Materials and Methods

2.1. Materials

The AlN powder with an average particle size of 1.1 μm used in the experiment was synthesized by carbothermal reduction and nitridation method in the laboratory. Its specific chemical composition is shown in Table 1. The sintering aid for aluminum nitride ceramics was yttrium oxide (Y₂O₃) powder (purity > 99.99%, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) with an average particle size of 3.1 μm. The surface modifier of AlN powder was octyltrichlorosilane (CH₃(CH₂)₇SiCl₃) (purity > 97%, Sigma-Aldrich, Milwaukee, WI, USA). The binder in the process of aluminum-nitride-powder formation was polyvinyl butyrate ester (PVB) (purity ≥ 99%, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) and the solvent was anhydrous ethanol (purity ≥ 99%, Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China). High purity nitrogen (purity ≥ 99.999%, Beijing Huanyu Jinghui City Gas Technology Co., Ltd., Beijing, China) and deionized water were also used.

Table 1. The specific chemical composition of AlN powder.

Elements	Al	N	O	C	Ca	Fe	Si
content	65.5%	33.5%	0.9%	0.06%	300 ppm	<100 ppm	<30 ppm

2.2. Surface Modification of AlN Powder

The schematic of obtaining the siloxane protective layer on AlN powder is shown in Figure 1. First, 100 g AlN powder was put into a rotating quartz tube and pumped to 10⁻⁹ Pa with a suit of vacuum systems. Then, the three-necked flask with 0, 0.2, 0.4, 0.6, 0.8, and 1.0 g octyltrichlorosilane was heated to 90 °C in the water bath, and the validated octyltrichlorosilane was slowly filled into the quartz tube with dry nitrogen.

When the pressure in the quartz tube was slightly higher than 1 atm, the exhaust valve was opened and the waste gas was vented into a 30 wt% sodium carbonate solution. After the octylchlorosilane in the flask was completely volatilized, the quartz tube was washed with dry nitrogen for another 30 min. The obtained powder was modified AlN powder. AlN powder modified with different doses of octylchlorosilane was labeled as M0, M1, M2, M3, M4, and M5, respectively. The AlN powder surface-modification device is shown in Figure 2.

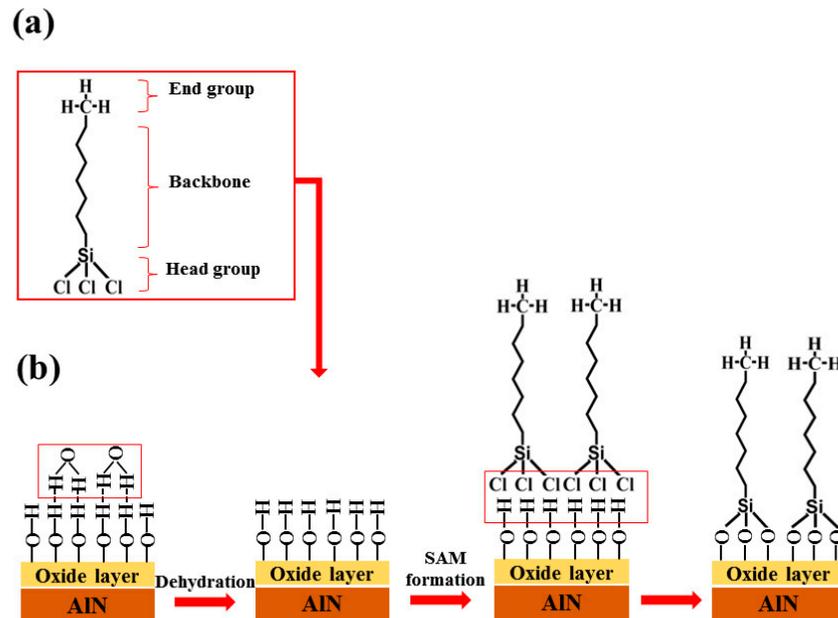


Figure 1. (a) Schematic of octyltrichlorosilane molecule indicating the headgroup, backbone, and end group. (b) Schematic of obtaining siloxane protective layer on AlN powder.

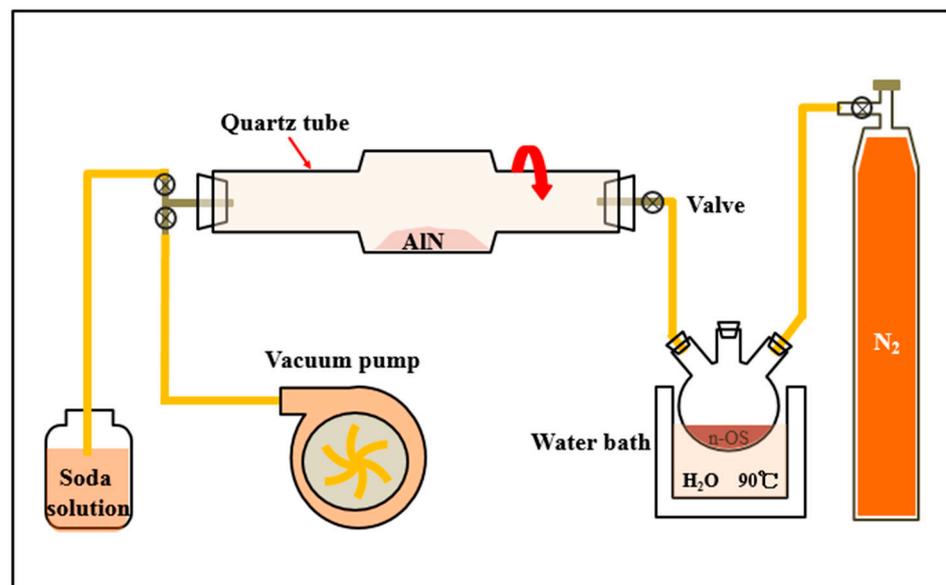


Figure 2. The surface modification device of AlN powder.

2.3. Preparation of AlN Ceramics

To evaluate the effect of surface modification on the thermal conductivity of AlN ceramics, 5 wt% Y_2O_3 powder was added to the modified AlN powder which had been stored in polyethylene bags for 1 year, and the mixed powder was mixed by ball-milling for 12 h with anhydrous ethanol as solvent, and the evenly mixed powder was granulated with

an anhydrous ethanol solution of 15 wt% PVB as the binder. Then, the granulated powder was pressed under 200 MPa to make samples with a diameter of 50 mm and a height of 5 mm. The above samples are placed in a Muffle furnace containing a boron nitride (BN) board for gel extraction. These samples were slowly heated to 500 °C and held for 2 h during gel extraction. Finally, the samples were put into a vacuum carbon tube furnace with flowing nitrogen. The temperature was heated to 1850 °C at the rate of 10 °C/min and held for 3 h. The AlN ceramics obtained based on the modified AlN powder which had been stored for 1 year were labeled as S0, S1, S2, S3, S4, and S5.

2.4. Characterization

The mass change of modified AlN powder in nitrogen atmosphere was characterized by thermogravimetric analysis (TG, Q5000IR, TA Instruments, New Castle, DE, USA), the grafting mass w_2 of octyltrichlorosilane was calculated according to the following formula:

$$w_2 = 2.19(w_1 - w_0) \quad (1)$$

where w_1 is the mass of octyltrichlorosilane grafted on AlN powders, w_1 is the loss mass of modified AlN powder during 200–500 °C, and w_0 is the loss mass of modified AlN powder during 200–500 °C.

The elemental composition of modified AlN powder was characterized by X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos, Manchester, Britain). The surface functional groups of modified AlN powder were characterized by Fourier infrared spectroscopy (FTIR, tensor X70, Bruker, Karlsruhe, Germany), The frequency range was 4000–400 cm^{-1} , The resolution ratio was 4 cm^{-1} . The surface hydrophobicity of modified AlN powder was evaluated by a water contact angle testing device (OCAH200, Dataphysics, Stuttgart, Germany). The phase composition of modified AlN powder in distilled water and AlN ceramics based on modified AlN powder was characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany). The thermal diffusivity of the AlN ceramics was measured by the laser thermal conductivity meter (LFA467, Netzsch, Selb, Germany), and its specific heat capacity was measured by the thermal analyzer (DSC, DSC3500, Netzsch, Selb, Germany). The thermal conductivity of aluminum nitride ceramics was determined according to the following formula:

$$\lambda = C_p \cdot \rho \cdot \alpha \quad (2)$$

where λ is the thermal conductivity of AlN ceramics, C_p is the specific heat capacity of AlN ceramics, ρ is the density of AlN ceramics, and α is the thermal diffusivity of the AlN ceramics. The Archimedes principle were used to characterize the bulk density and porosity of AlN ceramics, and the microstructure of the samples was also characterized using an electron microscope (SEM, Nova Nano450, FEI, Brno, Czech Republic).

3. Results and Discussion

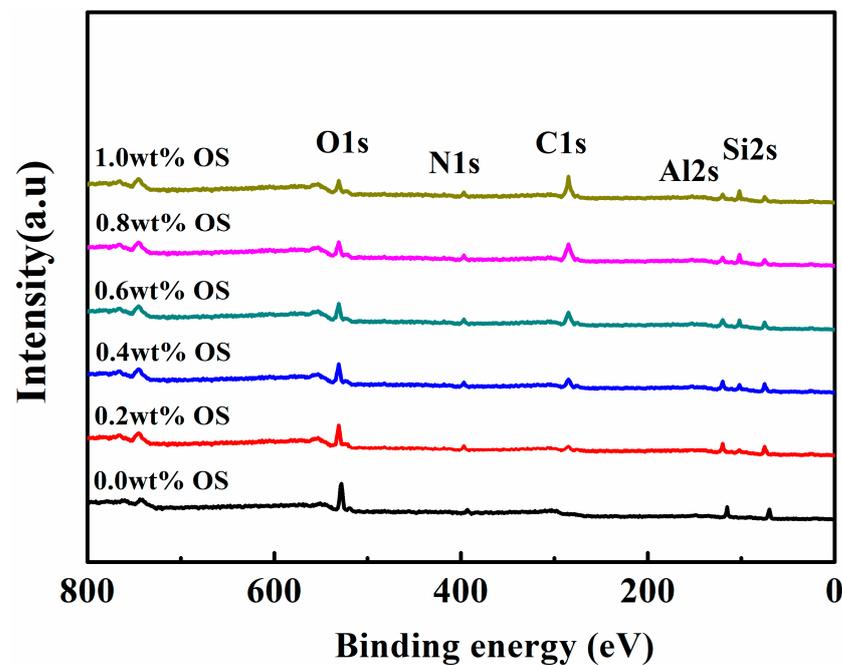
3.1. Surface Modification of AlN Powder

Table 2 shows the mass loss and grafting ratio of various OS-modified AlN powders. The pristine AlN powder exhibited a relatively large mass loss of 0.36 wt% from 50 to 250 °C, which was ascribed to the evaporation of physically absorbed water [24]. A slight mass loss of 0.21 wt% from 250 °C to 500 °C was ascribed to the decomposition of the hydroxyl [25]. For all modified AlN powder, there was less mass loss from 50 °C to 250 °C due to their enhance hydrophobicity as the increasing OS grafted on the powder surface. However, there was more mass loss from 250 °C to 500 °C resulting from the decomposition of as-grafted OS on the powder surface. The mass loss of the modified AlN powder at different stages indicated that octyltrichlorosilane has been successfully grafted on the surface of the AlN powder. In the current work, the grafting mass ratios of OS for the various AlN powders were estimated to be 0.0, 0.09, 0.26, 0.44, 0.63, and 0.81 wt%.

Table 2. Mass loss and the grafting ratio of various OS-modified AlN powder.

Samples	OS Content (wt%)	Mass Loss (%)		OS Grafting (wt%)
		50–250 °C	250–500 °C	
M0	0.0	0.36	0.21	0.0
M1	0.2	0.34	0.25	0.09
M2	0.4	0.33	0.33	0.26
M3	0.6	0.32	0.41	0.44
M4	0.8	0.30	0.50	0.63
M5	1.0	0.30	0.58	0.81

Meanwhile, the XPS spectra of various OS-modified AlN powders are displayed in Figure 3. The pristine AlN powder consisted of N, Al, and O elements; however, additional C and Si elements were found after modification. It is also obvious that the content of O, Al, and N elements gradually decreased, while the content of C and Si elements had a reverse tendency with increasing OS content (Table 3). Figure 4 shows the O1s of various OS-modified AlN powders. The peaks located at 531.4 and 532.8 eV were assigned to Al-O and Si-O, respectively [26,27] and the peaks centered at 532.8 eV increased as the increasing OS grafted on the surface of AlN powder. The chemistry of the modified AlN powder also verified that OS had successfully grafted on the surface of the AlN powder.

**Figure 3.** XPS spectra of various OS-modified AlN powder.**Table 3.** Surface elements abundance of various OS-modified AlN powder based on XPS.

AlN Powder	Surface Element Abundance (at%)				
	Al	N	O	C	Si
M0	50.12	32.47	17.41	-	-
M1	45.14	29.93	15.41	8.39	1.13
M2	41.76	24.74	13.41	17.90	2.19
M3	37.92	19.41	11.41	27.86	3.40
M4	25.87	15.93	8.06	44.65	5.49
M5	23.43	14.47	7.58	49.03	5.86

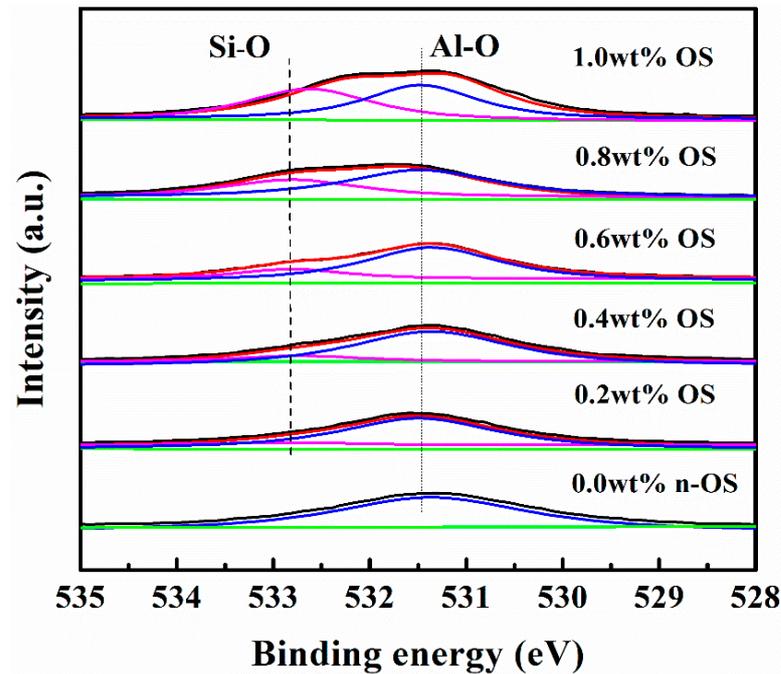


Figure 4. O1s of various OS-modified AlN powders.

To further understand the surface structure of OS-modified AlN powder, Figure 5 displays the FTIR spectra of various OS-modified AlN powders. There were three absorption peaks located at 698 cm^{-1} , 1326 cm^{-1} , and 3448 cm^{-1} . The peaks located at 698 cm^{-1} and 1326 cm^{-1} corresponded to the Al-N bond [28,29]; while the peak located at 3448 cm^{-1} was assigned to the O-H stretching vibration bond in the Al-OH compound [30]. After modification, new peaks located at 2931 cm^{-1} (-CH), 2852 cm^{-1} (-CH₂), and 1103 cm^{-1} (Al-O-Si) appeared [30,31]. The above results demonstrate that the OS grafted on the surface of AlN powder through the formation of the Al-O-Si bond.

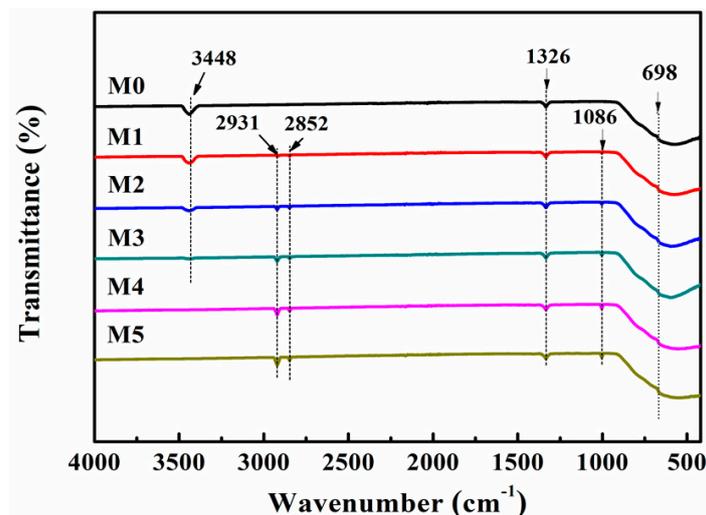


Figure 5. FTIR spectra of OS-modified AlN powder.

To investigate the effect of the siloxane protective layer on the surface polarity of AlN powder, a water contact angle was used to characterize the OS-modified AlN powder. Figure 6 shows the water contact angle of various OS-modified AlN powders. As shown in the figure, AlN powder is hydrophilic due to the existence of a large number of hydroxyl groups on its surface, and their water contact angle was only 34.8° ; however, the water

contact angles of AlN powder gradually increased to 65.2°, 97.5°, 122.4°, and 147.8° with the increasing OS content. When the OS content reached 1.0 g, the water contact angle of the powder slowly increased to 150.2°. The above results showed that the siloxane protective layer on the surface of AlN powder significantly improved its hydrophobicity

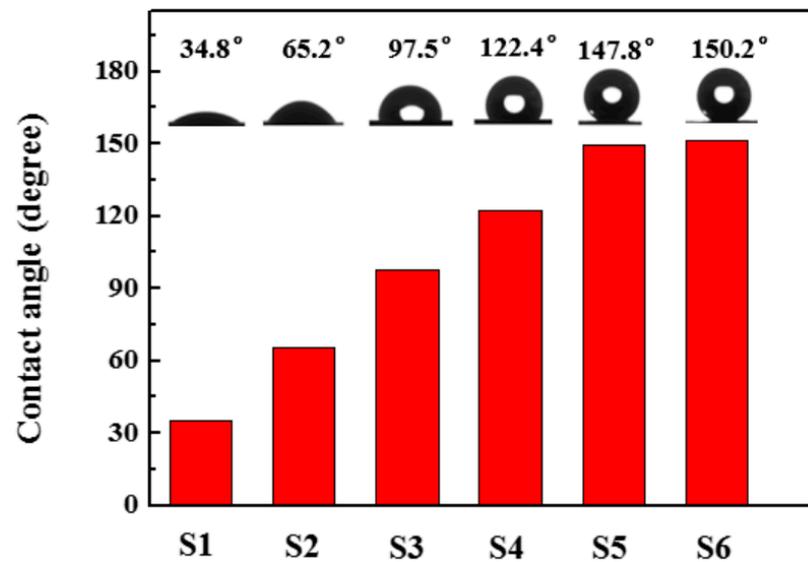
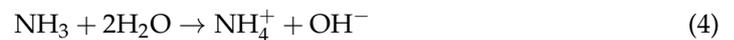


Figure 6. The water contact angle of various OS-modified AlN powders.

It is known that AlN will decompose rapidly and generates Al(OH)₃ when it is in contact with water [15,32]. The specific reaction process is shown in Equations (1)–(3).



Therefore, the stability of the siloxane protective layer in distilled water can be evaluated by measuring the hydration products of modified AlN powder. Figure 7 displays XRD patterns of modified AlN powder at 25 °C for 72 h. It can be seen from the figure that the hydration products of pristine AlN powder were mainly Al(OH)₃; however, with the increase in the octyltrichlorosilane content, the diffraction peak of Al(OH)₃ in the hydration products of modified AlN powder decreased rapidly, while the characteristic diffraction peak of AlN increased rapidly. When the content of octyltrichlorosilane reached 1 g, the phase of AlN powder did not change. The above results indicate that the siloxane protective layer on the surface of the modified AlN powder had good stability in distilled water, and effectively protected the AlN powder from decomposition. Its effect on improving the hydration resistance of aluminum nitride powder was similar to that of phosphoric acid and organic carboxylic acids [18,20].

Based on the above results we can conclude that a stable silane hydrophobic layer can be formed on the AlN powder surface by grafting octyltrichlorosilane, thereby improving the hydration resistance of AlN powder.

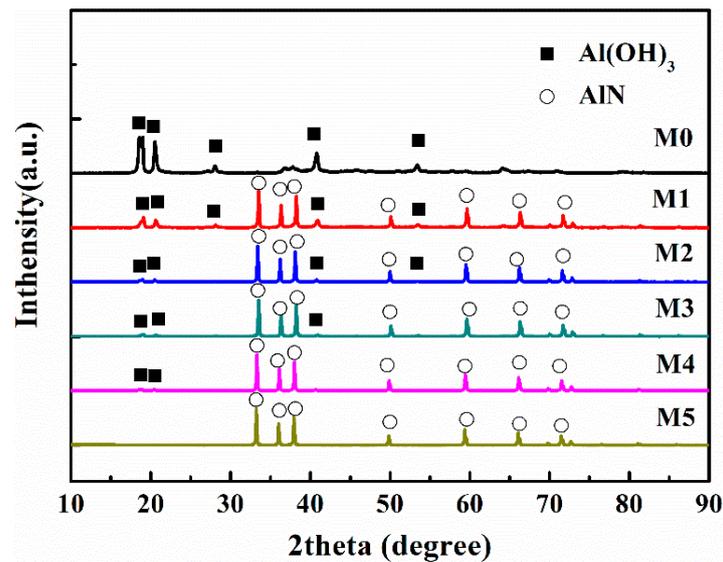


Figure 7. XRD patterns of modified AlN powder in 25 °C for 72 h.

3.2. Microstructure and Phase of AlN Ceramics

To investigate the effect of modified aluminum nitride powder on the microstructure and phase of aluminum nitride ceramics, Figure 8 displays the bulk density and apparent porosity of AlN ceramics prepared with modified AlN powder that had been stored for 1 year. It can be seen from the figure that although the content of octyltrichlorosilane grafted on the AlN powder surface increased, the AlN ceramics obtained based on the modified AlN powder had similar bulk density and apparent porosity. Their bulk densities reached 3.35, 3.34, 3.33, 3.33, 3.33, and 3.34 g/cm³, while their apparent porosities were 0.39, 0.38, 0.41, 0.39, 0.41, and 0.40%. These results indicated that the modified AlN powder had little influence on the porosity and bulk density of the AlN ceramics.

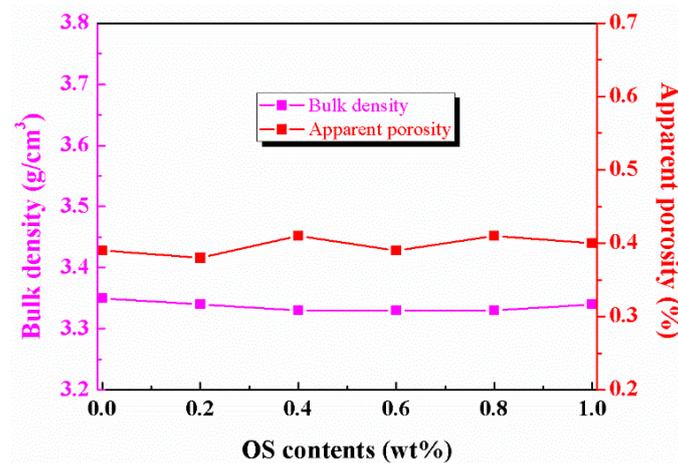


Figure 8. Bulk density and apparent porosity of AlN ceramics prepared with modified AlN powder stored for 1 year.

Figure 9 displays the microstructure of AlN ceramics prepared with modified AlN powder that had been stored for 1 year. As shown in Figure 9, there was little difference in the microstructure for AlN ceramics with various modified AlN powders. A small number of white grains were randomly located at the trigeminal grain boundaries of the gray grains. The EDS results showed that the gray grains only contained Al and N elements, and the atomic ratio was close to 1:1, which indicates that the gray grains were AlN, while the white grains were composed of Al, Y, and O elements, and the atomic ratio was close to 1:1:3,

which is YAlO_3 . To further clarify the composition and content of these phases, Figure 10 shows the XRD of AlN ceramics prepared with modified AlN powder stored for 1 year. The results once again confirm that the phase composition of aluminum nitride ceramics is AlN and YAlO_3 , and the content of these two phases is almost the same. However, the peak of AlN located at the (002) plane gradually shifted to the left as more octyltrichlorosilane was grafted on the AlN powder surface. The change in lattice constants was closely related to the content of oxygen impurities in AlN ceramics. According to the Bragg diffraction formula, $2d\sin\theta = n\lambda$, it can be deduced that as the content of octyltrichlorosilane grafted on the surface of AlN powder increased, the content of oxygen impurities dissolved in the AlN lattice reduced, and the interlayer space of the (002) plane became larger, leading to the peak shift to the left.

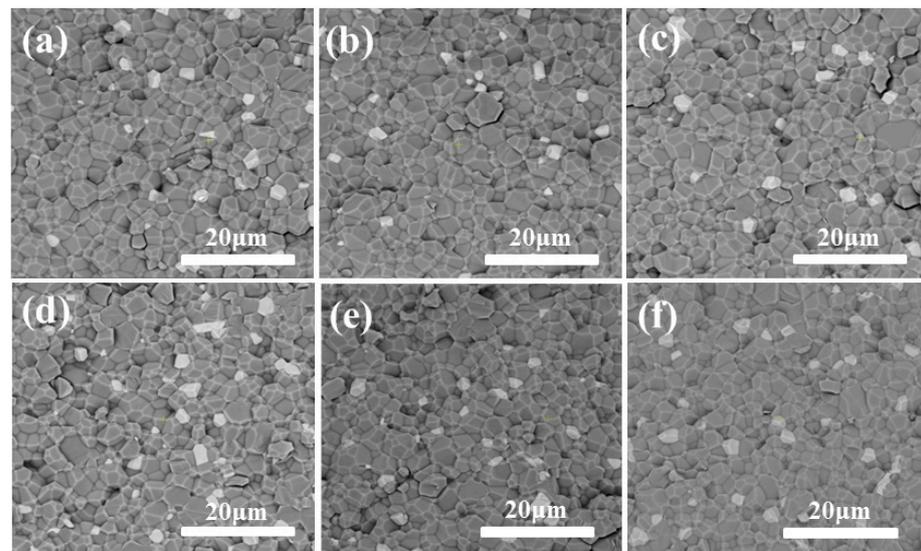


Figure 9. Microstructure of AlN ceramics prepared with modified AlN powder stored for 1 year. (a) Sample S0 (0.0 wt% OS), (b) sample S1 (0.2 wt% OS), (c) sample S2 (0.4 wt% OS), (d) sample S3 (0.06 wt% OS), (e) sample S4 (0.8 wt% OS), and (f) sample S5 (1.0 wt% OS).

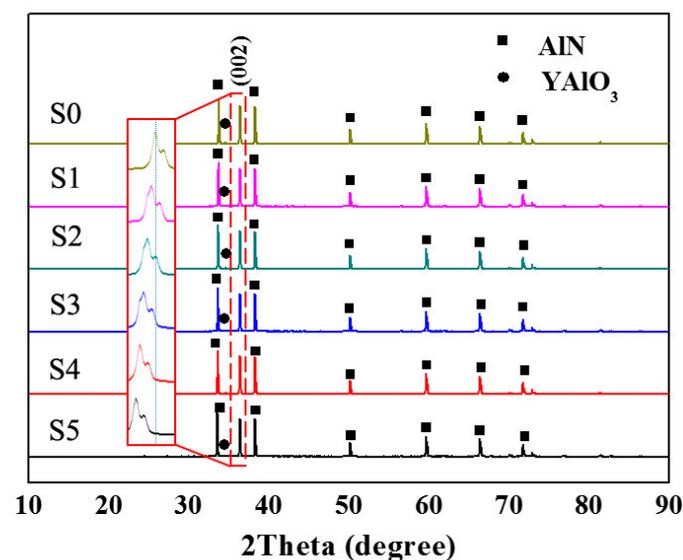


Figure 10. XRD of AlN ceramics prepared with modified AlN powder stored for 1 year.

These results illustrate that the modified AlN powder had little influence on the microstructure and phases of AlN ceramics, but it had great influence on the crystal structure of AlN.

3.3. Thermal Conductivity of AlN Ceramics

To further evaluate the effect of modified AlN powder on the thermal conductivity of AlN ceramics, Figure 11 displays the thermal conductivity of AlN ceramics prepared from modified AlN powder that had been stored for 1 year. The thermal conductivity of aluminum nitride ceramic based on the pristine AlN powder was only $143 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$; however, with the increase of octyltrichlorosilane, the thermal conductivity of AlN ceramics reached 151, 157, 172, and $181 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. When the OS dosage reached 1.0 g, the thermal conductivity of aluminum nitride ceramics reached $186 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The above results show that the siloxane protective layer grafted on the surface of the AlN powder was beneficial to improving the thermal conductivity of AlN ceramics.

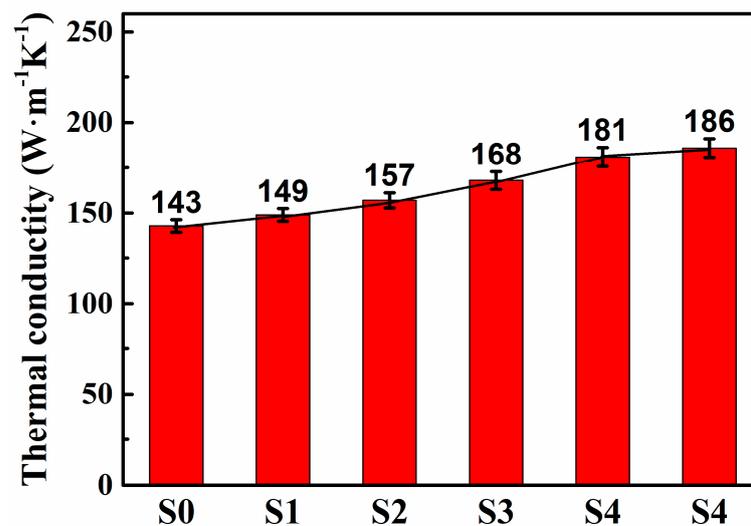


Figure 11. The thermal conductivity of AlN ceramics prepared based on modified AlN powder which has been stored for 1 Year.

4. Discussion

Based on the above results, it can be inferred that enhancing the hydration resistance of AlN powder through surface modification is very helpful for improving the thermal conductivity of AlN ceramics. The main reason is that the thermal conductivity of AlN ceramics is not only related to its microstructure and porosity, but also closely related to lattice defects caused by oxygen impurities in its lattice. Generally, this type of oxygen-related impurity defect has a transition point at an oxygen impurity content of 0.75 at%. Oxygen substitution onto a nitrogen site and the formation of aluminum atom vacancies occurs when the oxygen impurity content in the aluminum nitride lattice is lower than 0.75 at%, while extended defects such as inversion boundaries were generated when the oxygen impurity content in the aluminum nitride lattice is higher than 0.75 at% [33]. Unfortunately, aluminum nitride powder is prone to hydration during storage. This leads to an increase in the content of oxygen impurities in aluminum nitride ceramics and a decrease in thermal conductivity. Therefore, enhancing the hydration resistance of AlN powder is crucial for the stable preparation of high-thermal-conductivity aluminum nitride ceramics.

Octyltrichlorosilane is a silane coupling agent that is easily volatile at low temperatures. The octyltrichlorosilane reacts with the hydroxyl groups on the surface of AlN powder and is grafted onto the surface of AlN powder through Al-O-Si bonds. The good hydrophobic characteristics and structural stability of the silane protective layer can maximize the avoidance of contact between AlN powder and water, thereby maximizing the control of the oxygen impurity content in AlN powder in a stable range.

It is well known that there is a layer of aluminum oxide or hydrated aluminum oxide on the surface of AlN powder, which leads to the oxygen impurity diffusion from the surface to the interior of aluminum nitride grains under high temperature, forming

structure defects. Therefore, during the sintering process of aluminum nitride ceramics, it is often necessary to add sintering aids such as alkaline earth or rare earth to promote the densification of the ceramics and inhibit the diffusion of oxygen impurities into the interior of the grains. As Figure 9 shows, the aluminum oxide on the surface of AlN powder reacts with the sintering aid Y_2O_3 , forming a Y-Al-O glass phase at relatively low temperatures. Due to the material migration caused by the liquid phase being much faster than the solid phase diffusion, the liquid phase fills the voids of AlN ceramics and exists in the form of islands. At the same time, the formation of these liquid phases maximally inhibits the diffusion of oxygen impurities on the surface of aluminum nitride powder into the interior of the grains. Although the AlN ceramics obtained from different octyltrichlorosilane-modified AlN powder have little difference in bulk density, porosity, and microstructure, there is a great difference in crystal structure. The more the octyltrichlorosilane grafted onto the surface of AlN powder, the less the oxygen impurity content on the surface of AlN powder, and the fewer the oxygen impurity defects in the grains of AlN ceramics obtained based on these modified AlN powder, thereby greatly improving the thermal conductivity of AlN ceramics.

Based on the above discussion, it can be concluded that using octyltrichlorosilane-modified AlN powder as raw material can provide a simple, efficient, and practical method for the stable preparation of high-thermal-conductivity AlN ceramics.

5. Conclusions

In conclusion, high-thermal-conductivity AlN ceramics were successfully prepared based on octyl trichlorosilane-modified AlN powder. The siloxane protective layer grafted on the surface of AlN powder effectively avoided contact between the AlN powder and water. The siloxane protective layer not only enhanced the water contact angle of the AlN powder from 34.8° to 151° , but also ensured that the phase of the AlN powder did not change in 25°C distilled water for 72 h. AlN ceramics with thermal conductivity up to $186\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ were prepared based on the modified AlN powder which had been stored for one year. This work provides a simple, effective, and convenient method for the stable preparation of AlN ceramics with high thermal conductivity.

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