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^{27}Al High-Resolusion Solid-State NMR Study of Hydration of Ultrafine Powder of Aluminum Nitride

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Synopsis. ^{27}Al NMR spectra of hydrated aluminum nitride ultafine powder, measured using magic angle sample spinning technique, showed two peaks which can be attributed to Al coordinated by four N atoms and to Al coordinated by six O atoms, and the hydration process was discussed.

Aluminum nitride (AlN) is an attractive material as a substrate of electronic devices, since it has high heat-resisting property and large thermal conductivity.[1,2] Since high density is necessary to obtain the large thermal conductivity, ultrafine powder is promising to obtain a homogeneous and dense AlN substrate by sintering, but the powder easily reacts with atmospheric moisture to form a hydrated surface. The adsorbed oxygen-containing species leave their oxygen atoms after sintering, and the thermal conductivity is largely reduced by the oxygen.[2,3]

In the present work we have studied the hydration process of AlN ultrafine powder by means of ^{27}Al high-resolution solid-state NMR.

Experimental

Two kinds of AlN ultrafine powder were supplied by NEC Corporation; they are called Samples A and B, whose particle diameters are 100—1000 and about 2000 Å, respectively.

^{27}Al NMR spectra were obtained using magic angle sample spinning (MAS) technique by a JEOL FX-200 pulsed spectrometer at a resonance frequency of 52.00 MHz. The spinning speed was about 3.6 kHz. An ordinary one-pulse cycle was used with the flip angle of $\pi/6$ and the recycle time of 1 s. The shift values are referred to $AlCl_3$ aqueous solution. ^{1}H NMR spectra were also measured by a Bruker CXP-100 pulsed spectrometer, operating at a resonance frequency of 90.03 MHz, to obtain the hydrogen content. All the NMR measurements were performed at room temperature.

Results

Figure 1a shows an ^{27}Al MAS NMR spectrum of Sample A. Only one signal is observed at a position of 103 ppm with a width of 1.3 kHz. Other peaks are all attributed to spinning sidebands, which was confirmed by changing the spinning speed. ^{1}H NMR spectrum of this sample consists of two components with different linewidth; one is motionally-narrowed, and the other broadened by dipole-dipole interaction, being attributed to spatially fixed hydrogens. Total hydrogen content was estimated to be 0.71 wt%, while the content of the fixed hydrogens was 0.47 wt%

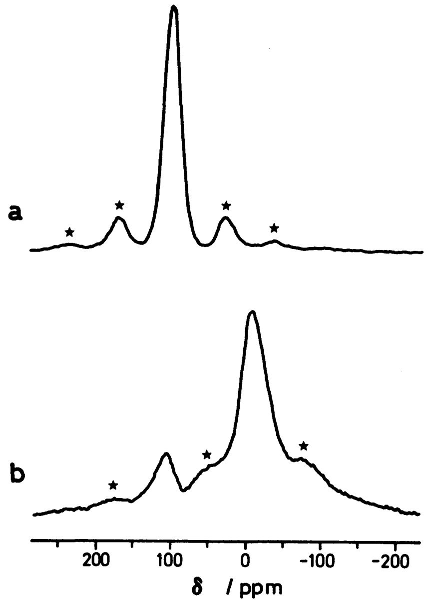

Fig. 1. ^{27}Al MAS NMR spectra of (a) Sample A and (b) Sample AH. The mark ★ denotes spinning sideband.

Figure 1b shows a spectrum of a heavily-hydrated sample of A (called AH). The hydration was carried out by exposing Sample A to liquid water at room temperature for 2 d. A new peak appears at −5 ppm with a width of 2.5 kHz, while the peak at 103 ppm slightly shifts to 109 ppm. Other peaks are attributed to spinning sidebands of the above two peaks. The hydrogen content is about 9.0 wt%, and the ^{1}H NMR spectrum shows a very narrow resonance line with a width of 350 Hz and a chemical shift of 5.2 ppm from tetramethylsilane. The shift value agrees with pure H_2O liquid (5.4 ppm),[4] and the line is motionally-narrowed. These facts suggest that most of the hydrogens are contained in the form of physisorbed H_2O left unreacted.

A dehydrated sample of A (Sample AD) was prepared by evacuating Sample A at 250 °C for 1 h. The hydrogen content is reduced to 0.17 wt%, and all hydrogens are spatially fixed. The ^{27}Al MAS NMR spectrum of this sample agrees with that of Sample A.

Sample B has a hydrogen content of 0.028 wt%, much lower than the other samples. The ^{27}Al MAS NMR spectrum agrees with that of Sample A again.

The results of ^{27}Al and ^{1}H NMR are summarized in Table 1.

Discussion

It is well-known that AlN reacts with H_2O in the following way:

$$AlN + 3H_2O \rightarrow Al(OH)_3 + 3NH_3. \tag{1}$$

In the AlN structure an Al atom is coordinated by four N atoms, while an Al atom is coordinated by six O

Table 1. Summary of ^{27}Al and ^{1}H NMR Results

Sample	Treatment	^{27}Al NMR		C_H[c]/wt%	
		Shift[a]/ppm	FWHM[b]/kHz	Total	Fixed
A	as supplied	103	1.3	0.71	0.47
AH	hydrated	−5 109	2.5 2.1	9.0	~0
AD	dehydrated	103	1.3	0.17	0.17
B	as supplied	103	1.3	0.028	0.014

a) Shift from $[Al(H_2O)_6]^{3+}$. b) Full width at half maximum. c) Hydrogen content.

atoms in $Al(OH)_3$. The coordination atom and their number are both changed by the reaction.

In the present work two signals are observed with different chemical shift values; 103 and −5 ppm. Since the hydrogen content is very low in Sample B, the number of Al atoms bonded with H via O is negligible. The signal observed at 103 ppm can therefore be attributed to the Al atom coordinated by four N atoms (abbreviated AlN_4). In the case of Al coordinated by O for aluminates and aluminum oxides, it is established that Al–O tetrahedra (AlO_4) and octahedra (AlO_6) have peaks in the range between 55 and 80 ppm and at about 0 ppm, respectively.[5] Consequently, the −5 ppm line can be assigned to AlO_6 in $Al(OH)_3$.

In a surface region, water reacts with AlN producing NH_3, and leaves surface hydroxyl groups. Some Al atoms may be connected with both N and O atoms. From the viewpoint of the Al coordination the reaction (1) is considered to proceed in the following steps:

$$AlN_4 \xrightarrow{a} AlN_xO_y \xrightarrow{b} AlO_6, \tag{2}$$

where $x+y=4$, 5, or 6. If considerable amounts of AlN_xO_y species were detected, it could be concluded that the reaction (2) proceeds step by step. Experimentally, however, no peaks were observed which can be attributed to AlN_xO_y. Namely, the step b is much faster than the step a.

Heavily hydrated sample, AH, has the two peaks, AlN_4 and AlO_6, indicating that the hydrated sample is a mixture of AlN and $Al(OH)_3$. The slight positive-frequency shift of the AlN_4 peak compared to Sample A is considered to be caused by superposition of the sideband of the AlO_6 peak, and hence it does not mean any structural change.

Samples A and AD have intermediate hydrogen contents between Samples B and AH. If oxygen-containing species such as OH and H_2O are assumed to be distributed homogeneously over all Al atoms, a considerable amount of Al atoms should be bonded to the O atoms. However, the amount of Al atoms bonded to O atoms is less than the detection limit, as shown in Fig. 1a. This fact suggests that oxygen-containing species are distributed over a limited amount of Al atoms.

In summary, the ^{27}Al NMR results demonstrate that the hydration reaction of aluminum nitride takes place quite inhomogeneously. Once an Al atom in AlN reacts with H_2O, the Al atom reacts with H_2O further more easily than the other Al atoms, finally forming $Al(OH)_3$. Consequently, the reaction product is a mixture of $Al(OH)_3$ and unreacted AlN, containing no detectable amounts of intermediate compounds.

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