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Research Article

Oxidation mechanism of aluminum nitride revisited

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Abstract: Different from the oxidation kinetics of other nitrides, the oxide layer on AlN can easily reach tens of micrometers at a temperature above 1200 ℃. In the present study, the oxidation mechanism of AlN is investigated through microstructure observation. The analysis indicates that the oxide layer is full of small pores. The formation of pores generates additional surface area to induce further reaction. The reaction thus controls the oxidation in the temperature range from 1050 to 1350 ℃. The oxidation rate becomes slow as the oxide layer reaches a critical thickness.

Keywords: oxidation mechanism; aluminum nitride; diffusion; reaction

1 Introduction

Among nitrides, aluminum nitride (AlN) is unique for its high thermal conductivity [1]. With the increasing demand for the miniaturization of consumer electronics, AlN has come to be used as a carrier for electronic components [2]. Prior to the bonding of electronic components, a surface modification of the AlN substrate is usually needed [3,4]. This is usually accomplished by an oxidation treatment [5,6]. However, the treatment may degrade the thermal conductivity of AlN [3]. The oxidation behavior of AlN is therefore an important issue.

The mechanism for the oxidation of AlN has been examined in many studies [7–16]. Previous studies mainly measured weight gain during oxidation [7–11,13–16]. The weight increase after oxidation of AlN bulk at lower temperature is very small, which may result in uncertainty in the measurement. Some research groups thus have investigated the oxidation of AlN powder [8,10,14,16]. Weight gain is indeed larger for the powder; however, the oxidation starts at lower temperature and the corresponding activation energy is also lower (see Table 1).

Table 1 also lists the oxidation mechanisms proposed in these studies. The studies agree that the oxidation mechanism is either a reaction process or a diffusion process. The reaction process usually takes place at lower temperature. For AlN powder, the reaction process is found during oxidation in temperatures ranging from 550 to 1100 ℃ [8,10,14,16]. For bulk specimens, the reaction process is found in the temperature interval from 1000 to 1390 ℃ [7,9,11–13, 15]. Diffusion during oxidation is found in the temperature range from 950 to 1150 ℃ for AlN powder [10,14], and from 900 to 1750 ℃ for bulk specimens [7,11,13,15]. Bellosi *et al.* [11] suggested that the diffusion is controlled by O^{2-} ions through the lattice or grain boundary.

While the previous studies agree upon the mechanism controlling oxidation, the reported values of activation energy show significant scatter from one study to another. For example, the activation energy varies from 67 to 366 kJ/mol for the reaction process [11,16], and from 160 to 423 kJ/mol for the diffusion

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Table 1 Previous results for the oxidation of aluminum nitride

Reference	Specimen + additive	Temperature (℃)	Atmosphere	Kinetics	Activation energy (kJ/mol)
Lavrenko and Alexeev [7]	Bulk	900–1100	Oxygen	Parabolic	255
Katnani and Papathomas [8]	Powder	700–900	Air	Linear	151
Sato *et al*. [9]	Bulk	1150–1250	Wet nitrogen	Linear	250
Suryanarayana [10]	Powder	800–1100	Air	Linear	188
	Powder	950–1100	Air	Parabolic	297
Bellosi *et al*. [11]	Bulk	1100–1390	Air	Linear	260
	Bulk+ Y_2O_3	1100–1250	Air	Linear	366
	Bulk+ CaC_2	1100–1200	Air	Linear	366
	Bulk+ CaC_2	>1250	Air	Parabolic	160
Robinson and Dieckmann [12]	Bulk	1000–1300	Air	Linear	347
Osborne and Norton [13]	Bulk	1150–1350	Air	Linear	175
	Bulk	1350–1750	Air	Parabolic	395
Brown and Norton [14]	Powder	850–950	Air	Linear	271
	Powder	950–1150	Air	Parabolic	423
Tseng *et al*. [15]	Bulk	1150–1450	Air	Parabolic	369
Zhou *et al*. [16]	Powder+ fluorides	550–700	Air	Linear	67
This study	Bulk+ Y_2O_3	1050–1350	Air	Linear	187

process [11–14]. Bellosi *et al*. [11] demonstrated that the activation energy of reaction increases from 260 to 366 kJ/mol after the addition of 3 wt% Y_2O_3. The variation of the reported values of activation energy is thus related to composition effects. Nevertheless, the activation energies for the systems of AlN–3%Y_2O_3 and AlN–2%CaC_2 are exactly the same when their oxidation is controlled by reaction (Table 1). To be demonstrated later, the oxidation kinetics of AlN is relatively fast, which has never been addressed before. In order to investigate the oxidation mechanism, detailed microstructure analysis is conducted in the present study.

2 Experimental

AlN (AN-170, 2 wt% Y_2O_3, Maruwa Co., Aichi, Japan) substrates with a thickness of 0.38 mm and a surface roughness (R_a) of 0.34 μm were used in the present study. The specimens were cleaned first in an ultrasonic bath of ethyl alcohol, then in one of acetone. Prior to the oxidation treatments, the substrate was heat treated at 500 ℃ for 4 h in air. This temperature was high enough to remove any organics, and low enough to induce noticeable oxidation [7,8,11,16]. The oxidation was carried out in a tube furnace. The AlN substrate was oxidized within alumina crucible. The purity of alumina crucible was higher than 99% Al_2O_3 to avoid the contamination. The oxidation was conducted at 1050, 1150, 1250, 1350, and 1450 ℃ for 1, 2, and 4 h in flowing air. The humidity in air was 3 ppm, as reported by the provider (Air Products Inc., Taipei, Taiwan, China).

To determine the extent of oxidation, the thickness of the surface oxide layer was estimated with electron probe micro-analysis (EPMA; JXA-8200, JEOL Co., Tokyo, Japan). Since the oxidation of AlN results from the reaction and diffusion of oxygen, the distribution of oxygen within the specimen was used as the evidence of oxidation. The EPMA technique can locate oxygen near the surface, and the thickness of the oxide layer was then estimated from maps of oxygen ions. The resolution of the technique was around 1 μm. A high-resolution transmission electron microscope (TEM; FEI Tecnai G^2 F20, Philips Co., Oregon, USA) was also used to characterize the microstructure. The TEM foil was prepared using an environmental dual-beam focused-ion-beam system (FIB; FEI Helios 600i, Philips Co., Oregon, USA). The phase analysis was conducted using X-ray diffraction (XRD; TTRAX-III, Rigaku Co., Tokyo, Japan).

3 Results

Figure 1 shows SEM back-scattered micrographs for the surface region of the oxidized substrates. Some white particles are found within the specimens. These particles are composed of Y, Al, and O as determined by EPMA. Figure 2 shows the XRD patterns of the specimens oxidized at various temperatures for 4 h. Only AlN (major) and YAG ($3Y_2O_3 \cdot 5Al_2O_3$, minor) are detected for the starting AlN substrate. According to the producer of the AlN substrate, the Y_2O_3 additive would react with the oxide layer on AlN particles to form YAG during hot-pressing. Since the amount of Y_2O_3 was low, 2 wt%, the amount of YAG is also low.

The α-Al_2O_3 phase is found after oxidation at 1050 ℃ for 4 h. The amount of Al_2O_3 increases with increasing oxidation temperature. From the width of the XRD peaks, the size of Al_2O_3 grains within the oxide

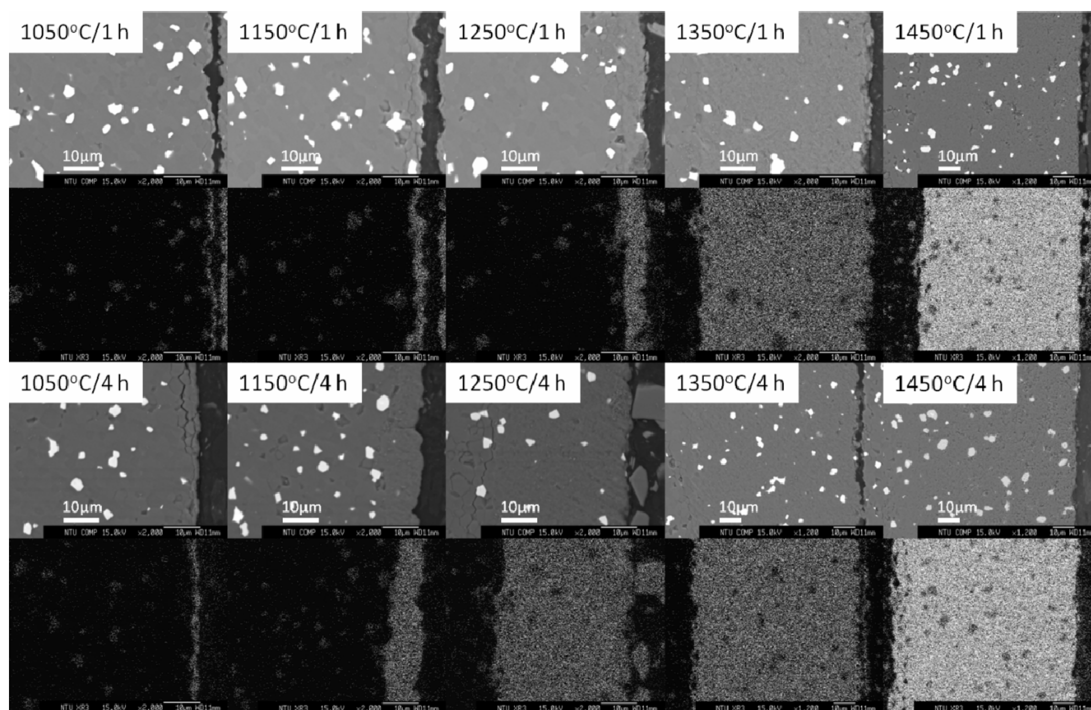


Fig. 1 SEM back-scattered micrographs for the surface region of oxidized AlN specimens and their corresponding maps of oxygen. Note that the magnification for micrographs of the specimens oxidized at 1350 ℃/4 h, 1450 ℃/1 h, and 1450 ℃/4 h is lower.

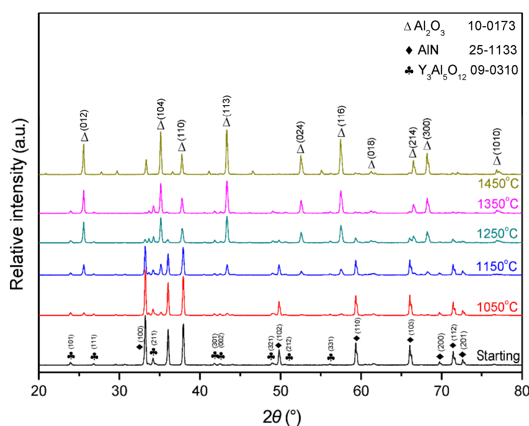


Fig. 2 XRD patterns for AlN specimens oxidized at various temperatures for 4 h.

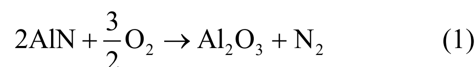
layer is around 40 nm for the substrate oxidized at 1050 ℃ and around 50 nm for the substrate oxidized at 1450 ℃.

Figure 3(a) shows a TEM micrograph of the AlN phase located within the substrate. Figure 3(b) shows a micrograph of the oxide layer. There are many pores within the oxide layer; the size of these pores is around 50 nm in length and around 20 nm in width. The long axis of the pores tends to be perpendicular to the surface of the substrate.

Figure 1 shows the mapping of the oxygen in the surface region. By assuming that the layer with oxygen is the oxidation product, the extent of oxidation can be estimated. More than three locations for each oxide layer were measured; the average and its standard deviation are shown in Fig. 4. The oxide layer is thin when the oxidation is conducted at 1050 and 1150 ℃. The layer increases its thickness rapidly as the oxidation temperature exceeds 1250 ℃. However, the thickness of oxide layer reaches its plateau after oxidization at 1450 ℃ for 2 h.

4 Discussion

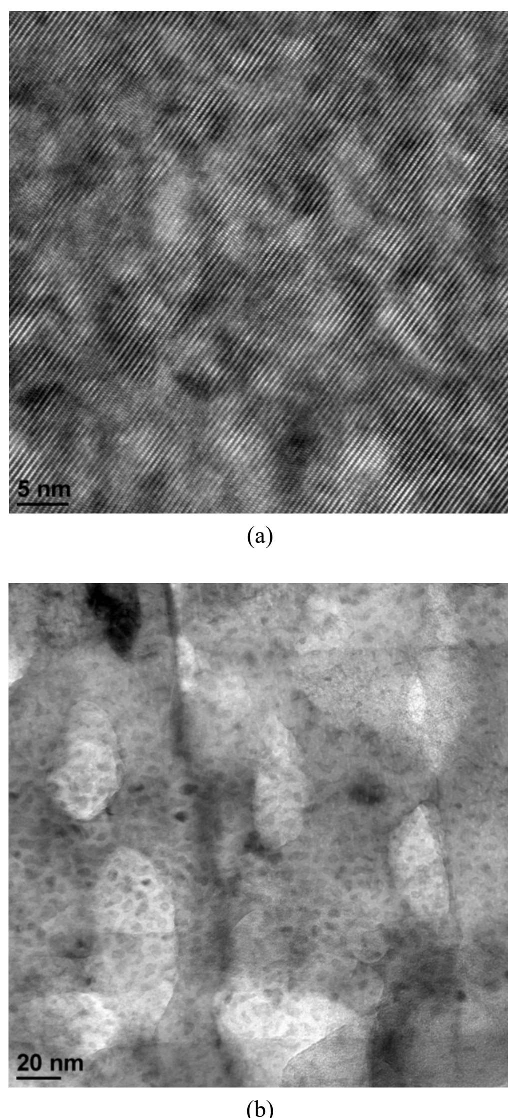
In the present study, the oxidation behavior of AlN substrates in the temperature interval from 1050 to 1450 ℃ is investigated. The oxidation is controlled by either reaction or diffusion. The reaction process involves the formation of nitrogen as shown in the equation below [9,17]:



$$2\mathrm{AlN}+\frac{3}{2}\mathrm{O}_2 \rightarrow \mathrm{Al}_2\mathrm{O}_3+\mathrm{N}_2 \qquad (1)$$

Due to the change from AlN to Al_2O_3, the above reaction is associated with a weight gain of 24%. The oxidation of AlN can therefore be monitored through the measurement of weight gain.

In contrast to the previous studies [7–16], the extent



(a)

(b)

Fig. 3 TEM micrographs for (a) AlN specimen and (b) oxide layer after oxidation at 1150 ℃ for 1 h.

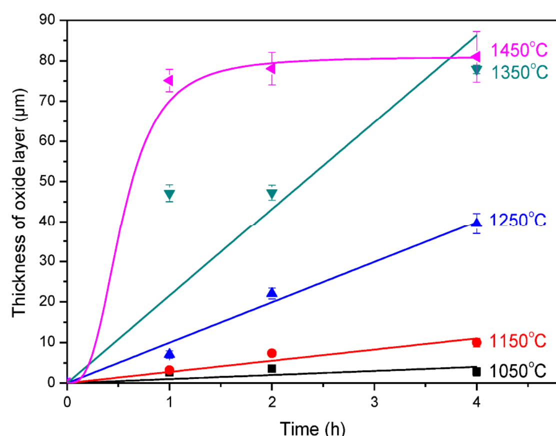
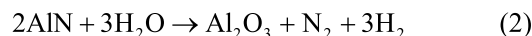


Fig. 4 Thickness of the oxide layer as a function of oxidation time at various temperatures. The thickness was estimated from the oxygen maps shown in Fig. 1.

of oxidation is determined through the measurement of the thickness of oxide layer (Fig. 4). The details of the microstructure of the oxide layer are revealed through the TEM analysis. Many pores are found within the oxide layer (Fig. 3(b)). Though the presence of pores within the oxide layer of AlN specimens was also observed in previous studies [9], their formation had been related to the presence of water in the oxidation environment as demonstrated by the following reaction [9]:



$$2\mathrm{AlN} + 3\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + \mathrm{N_2} + 3\mathrm{H_2} \tag{2}$$

However, the Gibbs free energy for reaction (1) is lower than that for reaction (2) in the temperature interval investigated [17]. Furthermore, the water content, or humidity level, in the oxidation environment of the present study is very low. The oxidation is likely controlled by reaction (1). In any case, the reactions (1) and (2) involve the formation of nitrogen.

The presence of pores confirms that the reaction is indeed taken place during oxidation. The reaction during oxidation forms a thick oxide layer.

Many nitrides are resistant to oxidation at elevated temperatures. For example, the thickness of oxide layer for a reaction-bonded silicon nitride (RBSN) is only 3 μm after oxidation at 1400 ℃ for 50 h [18]. Nevertheless, the thickness of the oxide layer on AlN reaches 45 μm after oxidation at 1350 ℃ for only 1 h.

The diffusion coefficients of $\mathrm{Al^{3+}}$ and $\mathrm{O^{2-}}$ ions through the lattice and grain boundary in aluminum oxide are well documented [19,20]. The following equations show one set of relationships for the diffusion coefficient of $\mathrm{Al^{3+}}$ ions through the lattice (D_l) and through the grain boundary (D_gb) [19]:

$$D_\mathrm{l} = 1.36\times10^{5}\exp\left(-\frac{577\,\mathrm{kJ/mol}}{RT}\right) \tag{3}$$

$$\delta D_\mathrm{gb} = 8.6\times10^{-4}\exp\left(-\frac{418\,\mathrm{kJ/mol}}{RT}\right) \tag{4}$$

In the above equations, δ is the thickness of the grain boundary, R the Boltzmann constant, and T the absolute temperature. Other reported values for the lattice diffusion coefficient (D_l) vary from 10^{-15} to 10^{-11} $\mathrm{cm^2/s}$ in the temperature range from 1100 to 1500 ℃, the boundary diffusivity (δD_gb) from 10^{-18} to 10^{-14} $\mathrm{cm^2/s}$ [19,20]. These values are very low, which suggests that no matter whether the diffusion is through the lattice or through the grain boundary, the diffusion distance should be on the order of 1 μm in the temperature range from 1000 to 1500 ℃. Nevertheless, the thickness of

the oxide layer reaches a value of 75 μm after oxidation at 1450 ℃ for 1 h (Fig. 4). Also note that there is a limit for the thickness of the oxide layer. For example, after the oxidation is conducted at 1450 ℃ for 1 h, the thickness of the oxide layer increases to 75 μm. It takes 3 more hours to increase from 75 to 81 μm.

The key to the oxidation of AlN is that the oxide layer is porous (Fig. 3(b)). The oxidation of AlN is accompanied by the formation of nitrogen as shown in reaction (1). The formation of small pores generates considerable fresh surface area to allow further reaction to take place. The oxide layer is therefore thick. However, the reaction is possible only when the exchange of nitrogen and oxygen is possible. In other words, the pore channel must allow the transportation of the gases. Figure 4 indicates that there is a maximum thickness for the oxide layer. This implies that the pore channels may be no longer available as the oxide layer is too thick. As the pores are not interconnected, only the diffusion of oxygen ions within the oxide layer is possible. The thickness increases slowly at elevated temperatures, mainly because the diffusion coefficient of ions in Al_2O_3 is small. From Fig. 4, the critical layer thickness is around 80 μm. To achieve such a thickness, oxidation at 1350 ℃ for 4 h or 1450 ℃ for 1 h is needed. Since the oxidation within the temperature range from 1050 to 1350 ℃ is a reaction process, it is possible to calculate its activation energy. The value for the activation energy is 187 kJ/mol. Our value falls within the range reported from the previous studies (67–366 kJ/mol in Table 1).

A schematic for the oxidation of AlN is shown in Fig. 5. The schematic illustrates the reaction involving the exchange of oxygen and nitrogen. Many small pores are produced by this reaction. The long axis of the pores thus tends to be perpendicular to the surface. The reaction process generates fresh surface area, facilitating further reaction. The increase in thickness of the oxide layer is therefore rapid. Diffusion may take place simultaneously within the thin oxide layer around each pore. However, the diffusion of aluminum and oxygen ions within aluminum oxide is so slow that the diffusion process contributes little to the thickness increase of the oxide layer.

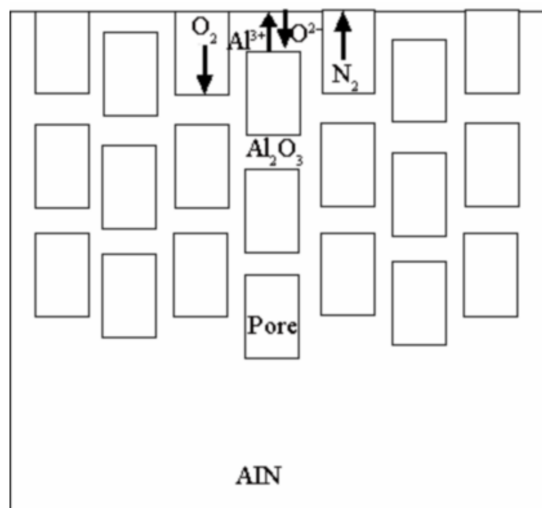


Fig. 5 Schematic showing the formation of the oxide layer during the oxidation of AlN. The oxidation process is mainly the reaction involving the exchange of N_2 and O_2.

5 Conclusions

With the help of microstructure analysis, the oxidation mechanism of AlN is investigated in the present study. The oxide layer formed on the surface of AlN substrate is a porous one. The oxidation kinetics is therefore fast. The reaction induces a rapid increase in weight and in oxide thickness, due to the formation of many pores. The reaction stops when the pores are no longer interconnected.

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