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Oxidation behavior of AlN substrate at low temperature

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The oxidation onset and the kinetics of polycrystalline AlN substrates were studied by measuring the weight percent of oxygen in the surface layer and the surface roughness with energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM), respectively. The oxidation started in the temperature range 800–900 °C and the entire surface of the AlN substrate was covered with an Al_2O_3 oxide layer below 1100 °C. The oxidation kinetics followed a linear rate law below 1000 °C and a parabolic rate law above 1100 °C. Above 1100 °C, the surface roughness increased abruptly by the irregular shape of overgrown oxide, which might enhance the adhesion of metal to the AlN surface in a metallization process. With an increase of the oxidation temperature above 1200 °C, the oxide layer split during cooling due to the thermal expansion mismatch between the AlN matrix and the Al_2O_3 oxide layer.

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1. Introduction

AlN substrates are very useful in the electronics and the optoelectronics industry for their high thermal conductivity, good electrical insulation [1], thermal expansion similar to silicon [2], and non-toxicity, unlike BeO. For many purposes, metallization of the AlN substrates is required. Oxidation of AlN substrates is known to be helpful for the adhesion of deposited metal layers, although the oxide film on the AlN substrate decreases the overall thermal conductivity [3, 4]. Therefore, the oxidation of AlN has received considerable attention, including topics such as onset of oxidation [2], oxidation kinetics [3–7], and change of surface morphology with oxidation [7].

The onset of AlN oxidation was studied with various methods. Geng and Norton [2] reported that the oxidation occurs at 800 °C via the Stranski–Krastanov mode by using transmission electron microscopy and electron diffraction. Yue *et al.* [8] used secondary ion mass spectrometry and X-ray diffraction to show that a continuous oxide can be formed when the oxidation time is extended to 20 min at 1100 °C. By electron energy-loss spectroscopy and high-energy electron diffraction it was determined that the growth rate law of the oxide surface layer of AlN is logarithmic [9].

The oxidation kinetics is generally known to follow a linear rate law below about 1000 °C and a parabolic rate law above that temperature [10]. The kinetics have usually been analyzed by measuring the mass change of the AlN substrate with oxidation, but the results differ from study to study [3–6]. The calculated activation energies for AlN oxidation also show a large scatter [10]. These differences appear to originate from the difference of the studied AlN materials, i.e. AlN powder, AlN single crystal, and AlN polycrystal. The chemistry of sintering aids like Y_2O_3 [11], the specific sintering procedure, and the oxidation environment may also be responsible for the observed differences.

In the present study, the oxidation behavior and kinetics of AlN ceramic substrates were examined by measuring oxygen weight percent change, instead of the mass change after oxidation, and the surface roughness change, using energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM), respectively.

2. Experimental procedure

The initial samples used in this study were 3 inch-diameter commercial poly-crystalline AlN wafers with 550 μm in thickness (STELLAR Insdustries, Inc.). Yttrium oxide had been added to the AlN powder as a sintering aid. Rectangular specimens $10 \times 10\,\mathrm{mm}^2$ in size were sawn from the wafers. Before oxidation, all specimens were ultrasonically cleaned in acetone and were weighed with a microbalance. The average density determined for all samples was $3.27\,\mathrm{g\,cm^{-3}}$, which is 98.5% of the theoretical value of $3.32\,\mathrm{g\,cm^{-3}}$ [12].

The thermal oxidation in air was conducted in a general furnace. The thermal oxidation temperature/time were 800 °C/1 h, 2 h, and 3 h to 1300 °C/1 h, 2 h, and 3 h with 100 °C intervals, respectively. After oxidation, the specimens were re-weighed and then their surface morphology and roughness were measured with AFM. The surface morphology and the chemistry change of the oxidized specimens were measured with SEM and EDX.

3. Results and discussion

3.1. Mass and roughness change with oxidation

As reported in the literature [3–6], the mass of the oxidized AlN substrate was expected to increase with increasing temperature. As can be seen in Fig. 1, the mass increase is significant for annealing above 1100 °C, while below 1100 °C the change is relatively small and even negative. Therefore, it was difficult to find the oxidation onset temperature and kinetics only by measuring the mass change.

The surface morphologies of the initial and oxidized specimens measured by AFM are shown in Fig. 2, which reveals that the AlN substrates consisted of many small grains with an average size of about 6 μm. Some of these grains were yttrium aluminum garnet, $Y_3Al_5O_{12}$(YAG) concentrated at the triple points of AlN grain boundaries, most probably during the sintering process [13]. The grains became exposed at the surface during the surface grinding process. After annealing up to 1000 °C each grain can be still identified in the figure, though the surface grain structure becomes ambiguous with oxidation above 900 °C. Above 1000 °C, individual surface grains can no longer be identified and the surface looks completely modified by the oxidation process.

The surface roughness changes with oxidation measured by AFM are shown in Fig. 3. In the figure, the oxidation begins in the temperature range 800–900 °C and the roughness increases continuously with an increase of temperature up to 1300 °C. The roughness increases abruptly at 1100 °C, similarly as in the case of mass change.

Therefore, from the results of the AFM analysis we derive the conclusion that the AlN substrates began to oxidize between 800–900 °C and that they were fully oxidized for annealing at 1100 °C for 3 h. The reason that oxidation of AlN substrates is usually helpful for metallization [3, 4] could be associated with the fact that the actual adhesion area of deposited metal layer would be increased by the continuous increase of surface roughness.

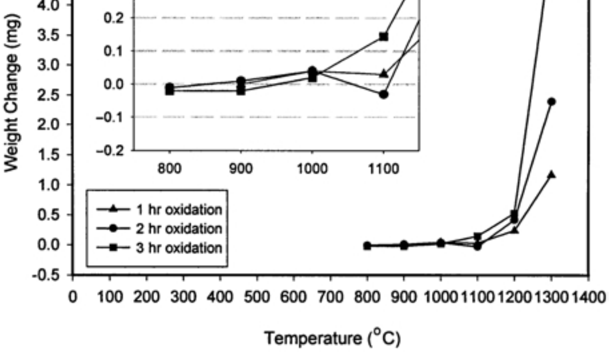


Figure 1 Weight change as a function of temperature and time for AlN samples oxidized at 800–1300 °C in 100 °C intervals.

3.2. Surface morphology of oxidized AlN matrix

The surface morphologies of AlN substrates after oxidation observed by SEM at various temperatures for 3 h are shown in Fig. 4. Fig. 5 is the magnified cross-sectional SEM images measured from cut-off edges of each specimen oxidized above 1000 °C, which shows an individual grain covered with oxide more clearly. Similar behaviors were also observed for the case of 1 h and 2 h oxidation. In Fig. 4a, which shows an image of 800 °C oxidation, the central grain shows several gray dots arranged in certain intervals, which looks like nucleation and growth of three-dimensional islands, as reported by Geng *et al.* [2]. The shape of the dots, however, is not triangular, as reported by Geng *et al.* [2], but circular. In Fig. 4b, the surface of AlN annealed at 900 °C, the oxidized area is expanded over more than 60% of the central grain surface area. After 1000 °C oxidation, in Fig. 4c and Fig. 5a, the entire area of the AlN substrate shows a rough surface, which means that the specimen was completely oxidized. For oxidation at 1100 °C, the surface begins to be over-oxidized and shows white threads on the surface in Fig. 4d. The threads are the connection of some overgrown oxide dots, which can also be identified in Fig. 5b for each AlN grain. At 1200 °C, the oxide layer is split after cooling as shown in Figs 4e and 5c and finally at 1300 °C in Fig. 4f, the oxide layer becomes widely opened and completely split as shown in Fig. 6.

The oxide threads on the surface and the split of the oxide layer are thought to arise from the different thermal expansion properties of AlN substrate and Al_2O_3 cover layer. The thermal expansion coefficients of AlN and Al_2O_3 are 4.5×10^{-6} and $8.8 \times 10^{-6}\,°C^{-1}$, respectively [4]. This mismatch acts as a driving force for the overgrown threads and the splitting of the oxide layer during cooling from the oxidation temperature.

The YAG phase formed as a reaction between AlN and yttrium oxide also showed some interesting behavior. Some of the YAG particles were released from the matrix during AlN oxidation and irregularly shaped holes were left behind. One of the observed surface holes is shown in Fig. 7. This phenomenon can also be explained by the thermal expansion differences between the AlN matrix, the Al_2O_3 oxide cover layer and the YAG particle. YAG particles consist of a mixture of Y_2O_3 and Al_2O_3 with a ratio of 5:3, which are known to lose their connection to the surrounding matrix after transformation from yttrium oxide via the sintering process [13]. The thermal expansion coefficient of Y_2O_3 is $8.3 \times 10^{-6}\,°C^{-1}$ and the coefficient of YAG lies between $8.3 \times 10^{-6}\,°C^{-1}$ and $8.8 \times 10^{-6}\,°C^{-1}$. If YAG particles were exposed to the bare surface without any barriers, they could be released easily by the mismatch of expansion between the three materials. If they were blocked by the AlN matrix or covered by the Al_2O_3 oxide layer, thus exposing only some parts to the bare surface, then they may not be released from the matrix.

3.3. Oxidation kinetics of AlN grains

Though only one hole is shown in Fig. 7, many similar holes were generated on the surface, even at 800 °C, by

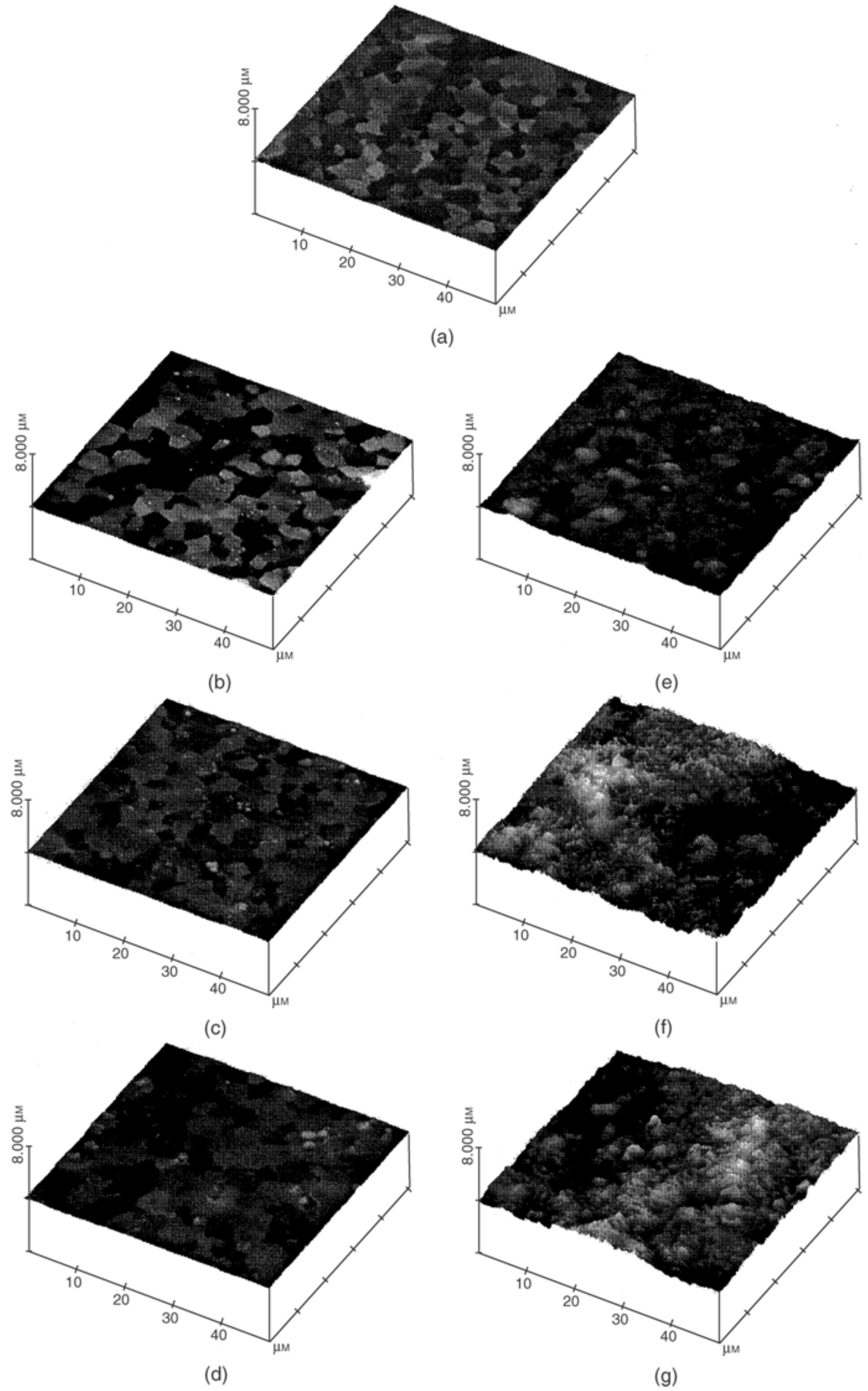


Figure 2 AFM images showing the surface morphologies of (a) initial AlN sample and oxidized samples for 3 h at (b) 800 °C, (c) 900 °C, (d) 1000 °C, (e) 1100 °C, (f) 1200 °C and (g) 1300 °C.

the release of YAG particles from the AlN matrix. This phenomenon might cause the decrease of mass with oxidation as shown in Fig. 1. Therefore, it becomes difficult to determine accurately any kinetics of AlN oxidation by measuring mass changes only.

We measured the oxygen content in the AlN matrix by EDX instead of mass change in order to exclude the mass decrease problem after oxidation and to analyze the kinetics of oxidation more precisely. As shown in Fig. 8, the change of oxygen content began at about 900 °C for 1 h oxidation, while 2- and 3-h oxidations the change began at 800 °C, abruptly increased at 1000 °C and was complete at 1200 °C. After the abrupt increase, the rate of oxygen content change becomes slower, which means that the surface is completely oxidized. Fig. 9 is a plot of oxygen content change as a function of time for different oxidation temperatures, which shows kinetics changing in the temperature range 1000–1100 °C. Below 1100 °C, the oxidation follows a linear rate law, but above 1100 °C, when the surface becomes completely covered

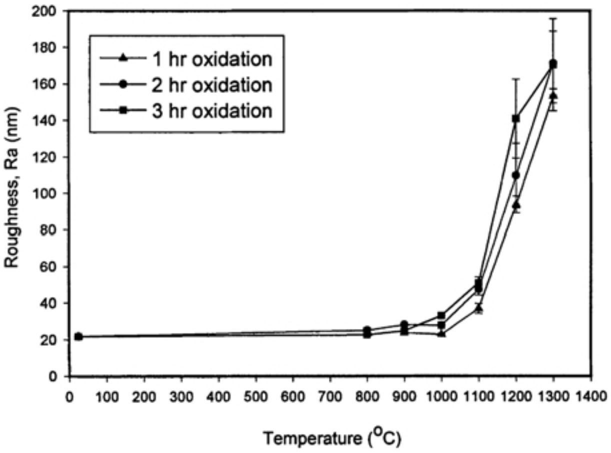
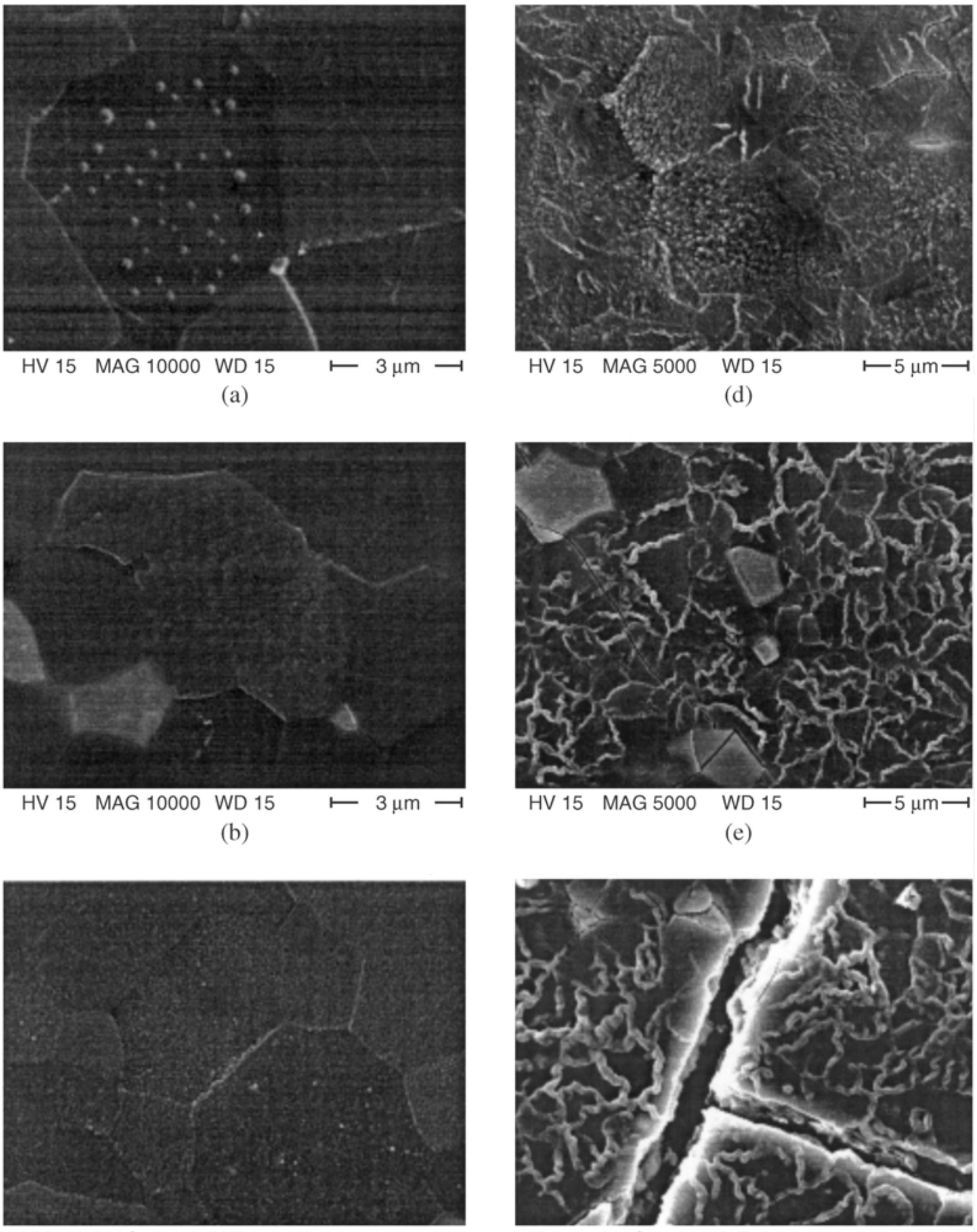


Figure 3 Surface roughness as functions of temperature and time of the oxidized AlN samples.

with an oxide layer, the kinetics changes to a parabolic rate law, because there should be interdiffusion between oxygen and aluminum elements through the oxide layer for further oxidation. Tseng *et al.* [5] measured the weight gain after oxidation using AlN substrates and reported that the parabolic oxidation begins above 1150 °C. Brown and Norton [10], Katnani and Papathomas [6], and Suryanarayana [14] reported that the oxidation follows a parabolic rate law over the range 850–950 °C using AlN powder. Our results are between these earlier results, but the activation energy could not be calculated using the weight percent change, because we did not get any reliable value of the weight gain after oxidation for the mass decrease problem after oxidation.



(a) (d) (b) (e) (c) (f)

Figure 4 SEM images of AlN samples oxidized at (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C (e) 1200 °C and (f) 1300 °C for 3 h.

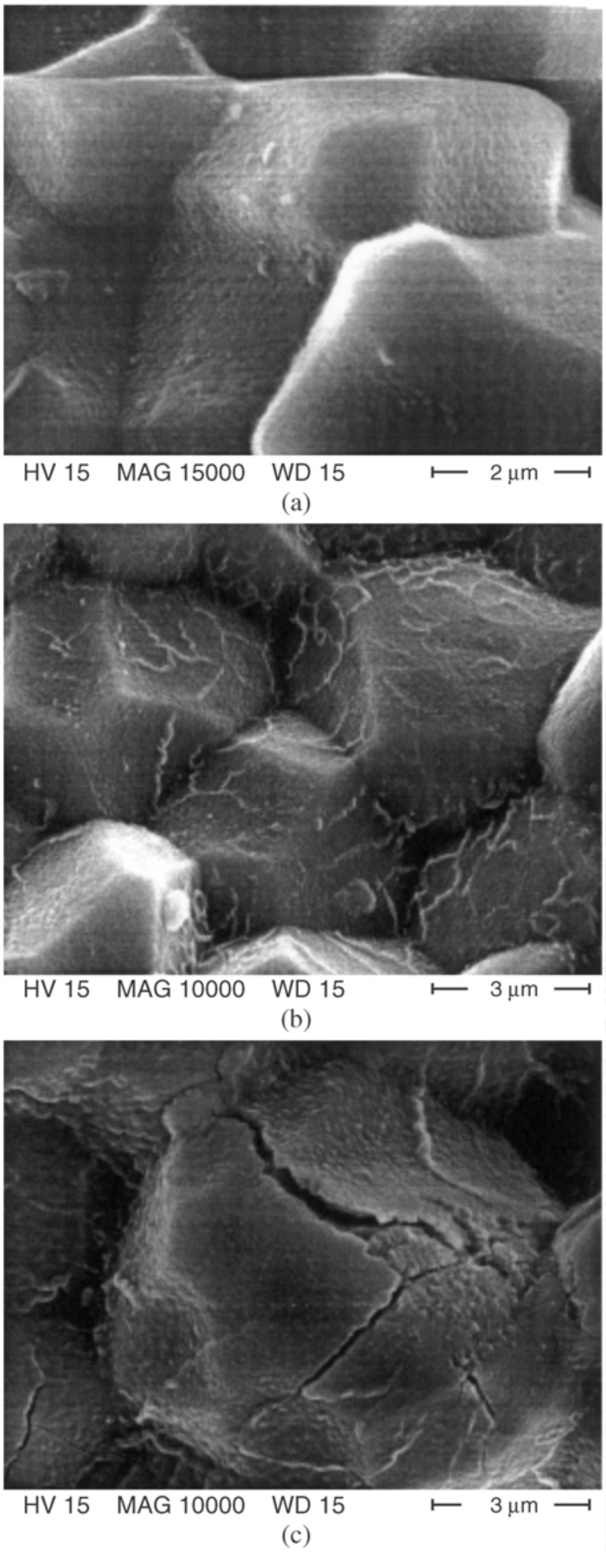


Figure 5 SEM images of AlN sample grains showing the oxidation and split of oxide layer of each AlN grain at (a) 1000 °C (b) 1100 °C and (c) 1300 °C for 3 h.

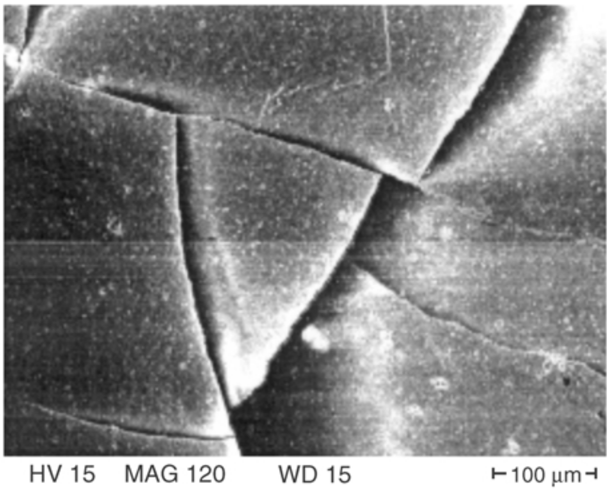


Figure 6 SEM image showing the split oxide film of an AlN sample oxidized at 1300 °C for 3 h.

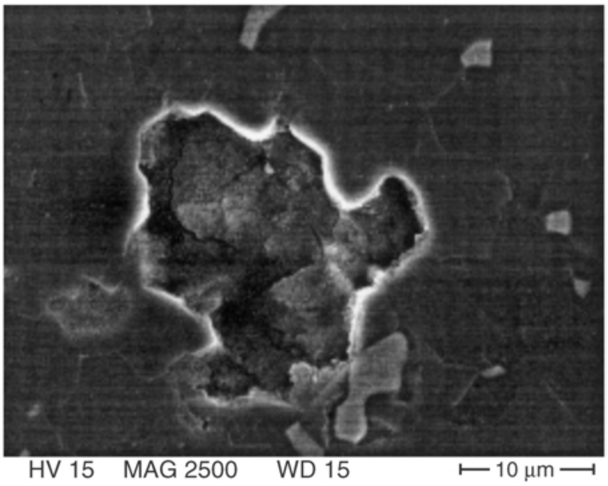


Figure 7 SEM image showing an irregular hole formed by the release of a YAG particle after an oxidation annealing for 3 h at 800 °C.

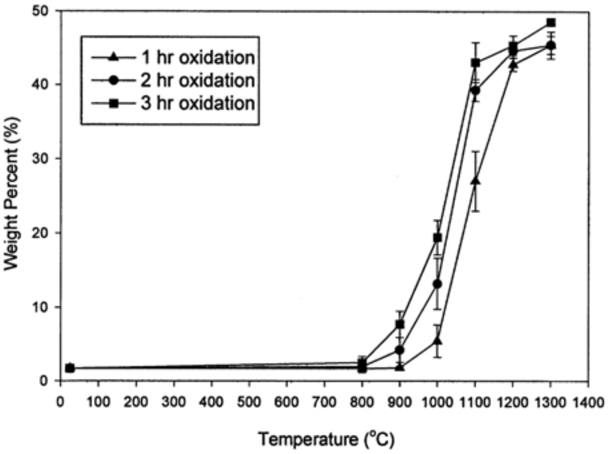


Figure 8 Oxygen content on the AlN surface measured by EDX as a function of temperature for different annealing times.

3.4. Behaviors of yttrium aluminum garnet particles

YAG particles showed some interesting features with oxidation, as demonstrated in Fig. 10. In Fig. 10a at 800 °C oxidation, some small dots can be found on the surface of YAG particles as on the surface of the AlN matrix in Fig. 4a. The YAG particles, however, changed into different shapes above 1200 °C, as shown in Fig. 10b. Based on the figure, it appears that the AlN oxidation process also affected the YAG particles. As mentioned, some of YAG particles that were not released from the matrix after oxidation are exposed to the strain

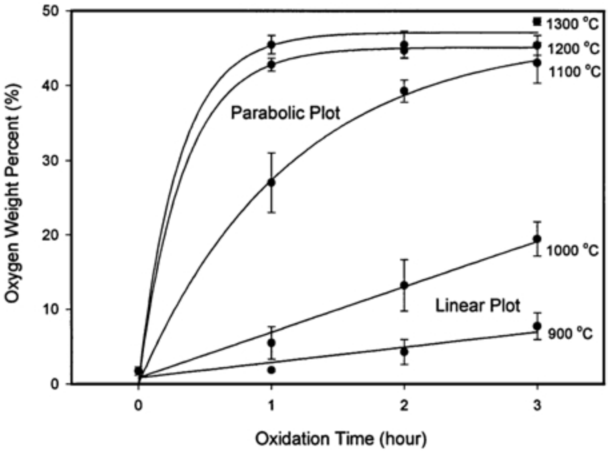


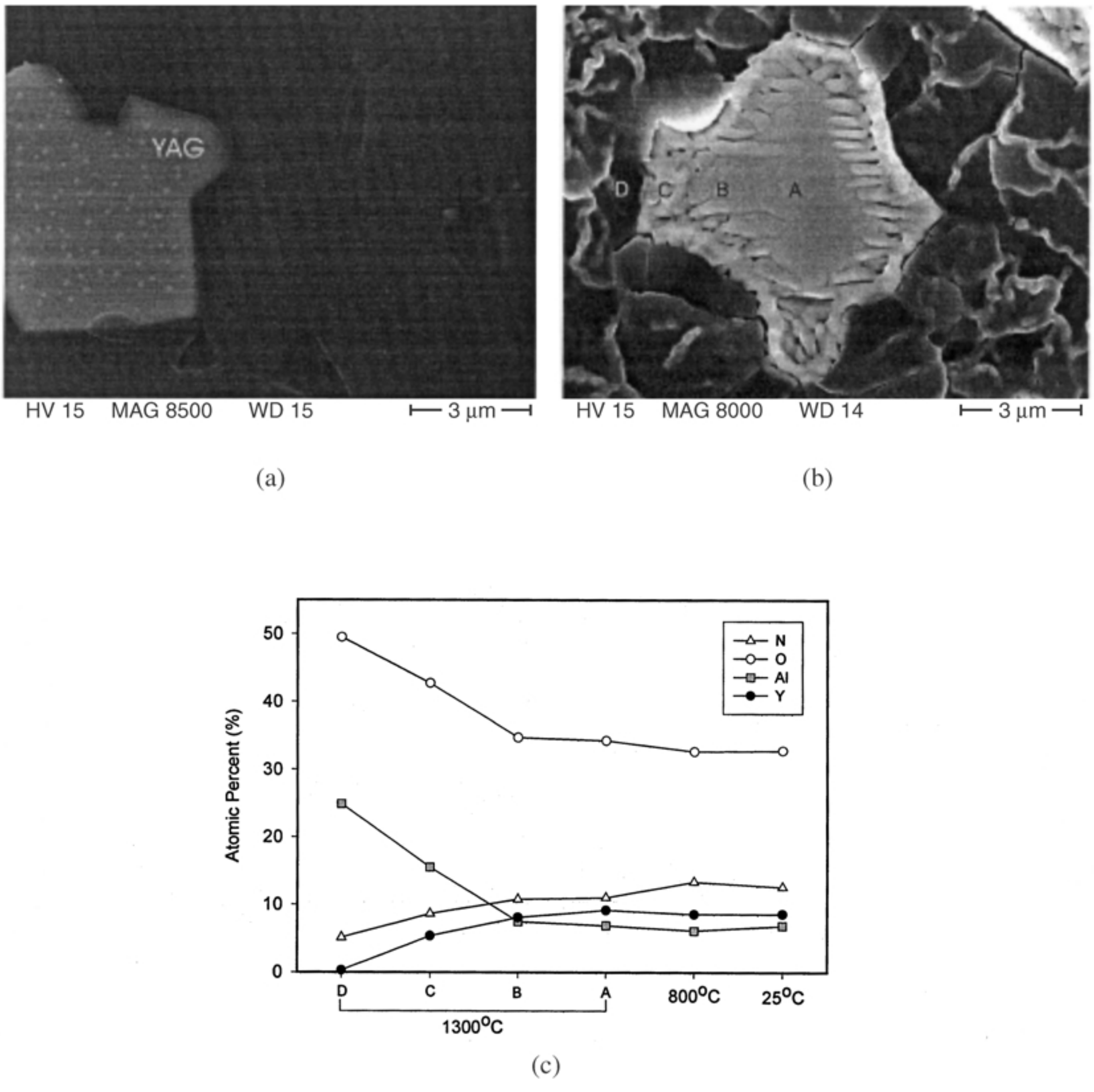
Figure 9 Plot of oxygen content measured by EDX as a function of time for different temperatures. The two lower results follow a linear rate law, while the three upper results follow a parabolic rate law.

field at their boundaries with the AlN matrix. The strain might cause the diffusion of some elements across the boundary. Fig. 10c shows the atomic percent changes of four major elements at four different positions indicated in Fig. 10b with two references, suggesting that exchange of yttrium and aluminum and the nucleation of a new phase took place at the boundary and new phases grew from the boundary into the YAG particle. EDX shows a stoichiometric YAG phase in the middle (points A & B) of the figure, while at the edge (point C) a new phase is growing, which may be of $AlY_xO_yN_z$ composition. The nitrogen content at point D is lowest, because of the oxygen and nitrogen exchange between the AlN matrix and air environment with the oxidation process [6].

4. Conclusion

AlN polycrystalline substrates were oxidized in a general air-environment furnace at various temperatures up to 1300 °C. Surface morphology changes and oxidation kinetics were studied using AFM, SEM and EDX. AlN began to oxidize at 800 °C and the entire AlN surface was covered with an oxide layer at 1000 °C. The surface roughness increased continuously from 900 °C.

Because of the thermal expansion mismatch of the AlN substrate and the Al_2O_3 oxide layer, the surface oxide layer splits during cooling after oxidation at a temperature of 1200 °C and higher. Most $Y_3Al_5O_{12}$



(a)

(b)

(c)

Figure 10 SEM image showing (a) small dots on the surface of an YAG particle and (b) an irregular boundary shape of a YAG particle after oxidation at 800 °C and 1300 °C for 3 h, respectively and (c) a plot of atomic percent measured by EDX of four major elements at four points of (b) with two references as a function of position within the YAG particle.

(YAG) particles revealed at the surface during the polishing process are easily released from the surface, possibly also because of thermal expansion differences. This effect causes the study of oxidation kinetics via mass change measurement to be difficult and unreliable. Therefore, we measured the oxygen content of the AlN matrix by EDX to exclude this uncertainty. EDX analysis revealed that below 1100 °C the oxidation followed a linear rate law, and above 1100 °C the rate became parabolic. YAG particles were also affected as temperature increased and a new phase of composition $AlY_xO_yN_z$ grew from the interface between YAG particle and AlN matrix by the diffusion of Al from the AlN matrix.

Acknowledgment

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