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One role of titanium compound particles in aluminium nitride sintered body

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Microstructure of titanium compound particle in polycrystalline aluminium nitride (AlN) has been investigated using micro-auger electron spectroscopy (μ-AES). AlN–0.5 wt% TiO_2–1.5 wt% Y_2O_3–0.4 wt% CaO system was sintered at 1850 °C in nitrogen atmosphere using a graphite furnace. The AES studies show that the composition of the titanium compound particle is titanium, aluminium, carbon, oxygen, nitrogen and calcium. On the other hand, no calcium is observed by AES in the AlN grains and grain boundary. It is found that one role of the titanium compound particle is to trap calcium included in polycrystalline AlN.

1. Introduction

AlN has high thermal conductivity (its theoretical value is 319 $W\,m^{-1}\,K^{-1}$ at room temperature [1]), high electrical resistivity (10^{13} Ω cm), and high mechanical bending strength (300 MPa). These excellent properties makes it an attractive candidate for packaging materials used in integrated circuits (IC) [2].

In a previous study [3], we investigated the microstructure of AlN–0.5 wt% TiO_2–1.5 wt% Y_2O_3 system, which was prepared by powder sintering, using μ-AES, which can analyse small regions about 30 nm in diameter and 5 nm in depth, and found that the titanium compound particles distributed in the AlN sintered body contained calcium although no calcium was added during the fabrication process. It was suggested that the titanium particles might be playing the part of trapping calcium present as impurities in the raw materials.

Greil *et al.* [4] reported that a calcium compound, which is added as a sintering aid in AlN, diffuses along the grain boundary and vaporizes from the sample surface on annealing at 1850 °C in carbon-containing nitrogen atmosphere.

In AlN doped with both titanium and calcium compounds, calcium should be included in the titanium compound after sintering in a carbon-containing atmosphere and most of the calcium vapor from the sample should be present if the titanium compound acts to trap calcium.

The purpose of this paper is to investigate the microstructure of the titanium compound distributed in polycrystalline AlN, which is doped with both TiO_2 and CaO, using μ-AES and to clarify the role of the titanium compound with regard to begin calcium trap.

2. Experimental procedure

AlN powder with a specific surface area of 3.3 $m^2\,g^{-1}$, 0.5 wt% of TiO_2 powder, 0.4 wt% of CaO powder, and 1.5 wt% of Y_2O_3 powder as a sintering aid were mixed in ethyl-alcohol for 3 h. The concentration of these raw powders is displayed in Table I. The raw titanium powder included no calcium as impurities as shown Table I. The mixture was moulded into a pellet shape, 12.5 mm in diameter and 4 mm in thickness, using a stainless steel die. Sintering was performed at 1850 °C for 5 h in nitrogen atmosphere using a graphite furnace to vaporize calcium from the sample [4].

The composition of the sintered sample was estimated using X-ray diffraction (XRD) (RU-300, Rigaku, Japan). A XRD pattern was obtained in the range of $2\theta = 20°$ to 80 °C using a Copper target (CuK_α) at room temperature.

To measure the concentration of calcium in the sintered sample, an inductively coupled argon plasma emission spectrophotometer (ICP; Model 1200VR, SEIKO, Japan) was used.

The AlN sintered body was fractured to about 5 mm in size to investigate the titanium compound distributed in the sintered AlN sample by μ-AES. The μ-AES (Model PHI-670 PERKIN ELMER, USA) studies were performed with an accelerating voltage of 3 kV, electric current of 1 nA and electron beam size of 80 nm and under 1×10^{-7} Pa. Depth profiles were obtained with Ar-ion etching at 16 $nm\,min^{-1}$ in the AES system.

A nitrogen peak appeared in the AES spectrum overlapping with one of titanium peaks which corresponds to the $L_3M_{2,3}V$ transition [5], so the intensity of the nitrogen peak is evaluated by the following method.

Fig. 1 shows an AES spectrum obtained from the TiO_2 sample. One can see two peaks caused by titanium labelled Ti-1 and Ti-2 in Fig. 1. The first peak,

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TABLE I Composition of impurities in the raw powders

	O (wt %)	C (wt %)	Ca (p.p.m.)	Si (p.p.m.)	Fe (p.p.m.)	Cr (p.p.m.)	Ni (p.p.m.)	Mg (p.p.m.)	Sr (p.p.m.)
AlN	0.95	0.04	27	10	< 10	–	–	–	–
Y_2O_3	–	< 0.4	< 10	–	< 4	–	–	–	–
TiO_2	–	–	–	–	45	4	1	–	–
CaO	–	–	–	–	10	–	–	300	100

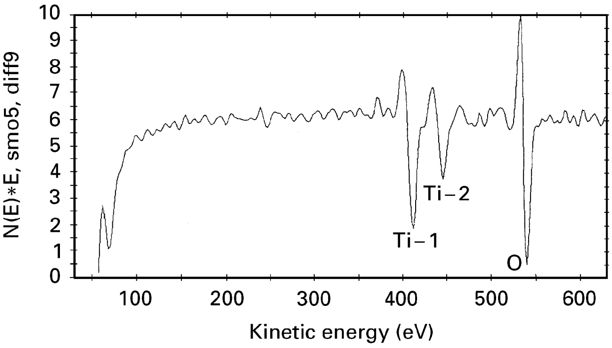

Figure 1 AES spectrum obtained from TiO_2. Two peaks caused by Ti, labelled Ti-1 and Ti-2, can be observed.

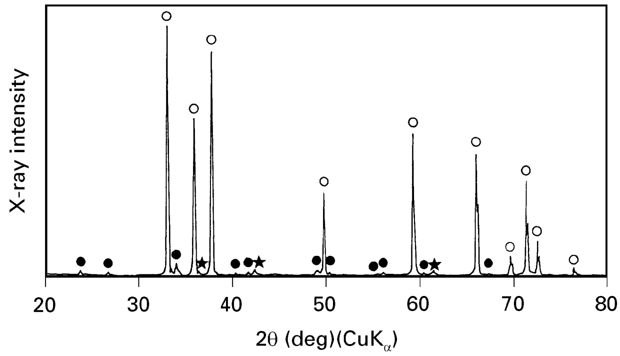

Figure 2 XRD pattern obtained from the sample. AlN is observed as a major crystalline phase, and $Y_2O_3 \cdot Al_2O_3$ and titanium compound phase such as TiO or TiN is observed as a minor crystalline phase. Key: ○ AlN; ● $Y_2O_3 \cdot Al_2O_3$; ★ TiN or TiO.

labelled Ti-1, corresponds to the $L_3M_{2,3}V$ transition and the next peak, labelled Ti-2, is caused by the L_3VV transition [5]. The intensity ratio of these peaks ($I_{Ti\text{-}1}/I_{Ti\text{-}2}$) is estimated at 1.75. Thus, when a nitrogen peak overlaps the titanium peak in the obtained AES spectrum, the intensity of nitrogen is evaluated by the following equation,

$$I_N = I_{N,Ti} - 1.75 \times I_{Ti}$$

where $I_{N,Ti}$ represents the intensity of overlapped peak of nitrogen and titanium, and I_{Ti} represents the intensity of titanium which corresponds to the L_3VV transition.

3. Results and discussion

3.1. XRD study

The obtained AlN sample has a relative density of over 99.9% and appears black. Fig. 2 shows the XRD pattern obtained from the AlN sintered body. The peaks in the XRD pattern are labelled using JCPDS cards (No. 25-1133, No. 33-41, No. 38-1420, No. 23-1078), AlN (hexagonal, P63mc), Y_2O_3–$A1_2O_3$ (orthorhombic, Pnma), and TiN or TiO. The obtained XRD study could not determine whether the composition of the titanium compound has either TiN or TiO since both TiN and TiO have the same crystal structure as rock salt [6]. In a previous study [3, 7], we found that the composition of the titanium compound was Ti–Al–O–N–C in AlN–0.5 wt % TiO_2–1.5 wt % Y_2O_3 system using energy dispersive X-ray analysis and AES. In this study, the titanium compound is thought to have a similar composition as the sample obtained in the previous study since the obtained sample in this study is prepared under the same conditions except for doping with CaO.

We observed no calcium compound phase such as CaO–Al_2O_3. The quantity of calcium in the sample was estimated at 0.004 wt % by ICP measurement and this was too small for detection by XRD. A large quantity of calcium is thought to vaporize during sintering. Greil indicated that the calcium evaporates from the sample surface on annealing in a carbon-containing nitrogen atmosphere by the following reaction [4].

$$CaAl_2O_4(l) + N_2(g) + 4C(g) \rightarrow 2AlN(s) + 4CO(g) + Ca(g) \quad (1)$$

In this study, the same reaction given in equation (1) is thought to occur since sintering was performed using a graphite furnace, giving conditions similar to those in Greil's study [4].

3.2. AES study

Fig. 3 shows the scanning electron microscope (SEM) image obtained from the fractured sample. One can see that the AlN sintered body is fractured at the grain boundaries. Fig. 4a and b show the AES spectra obtained from the AlN grain and the small particle, labelled A and B in Fig. 3, respectively. Fig. 4a obtained from the AlN grain indicates that its composition is aluminium, nitrogen and oxygen. Fig. 4b obtained from the small particle shows that its composition is aluminium, calcium, nitrogen and titanium. Both calcium and titanium can be observed in the small particle. It is suggested that the titanium compound traps calcium since calcium can be observed in the titanium compound and not in the AlN grain.

Fig. 5 shows a SEM image obtained from the same sample. This SEM image shows that the AlN grain, labelled A in Fig. 5, is fractured in the AlN grain (not at the grain boundary) and a small particle, labelled

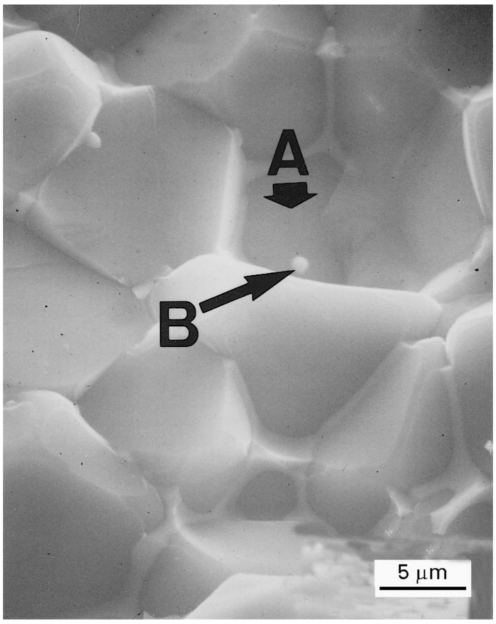

Figure 3 SEM image obtained from the fractured sample. One can see that the AlN, labelled A, is fractured at the grain boundary and the small particle labelled B, exists on the grain boundary.

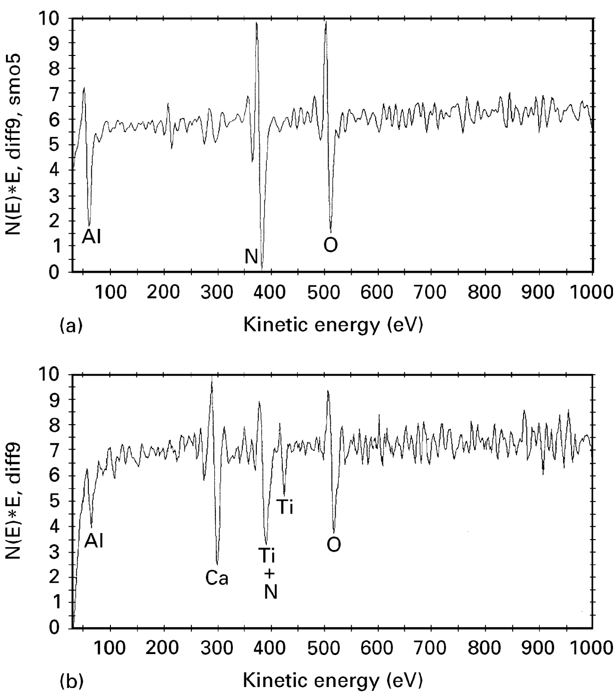

Figure 4 AES spectra obtained from various positions. (a) and (b) are obtained from the AlN grain labelled A in Fig. 3 and the small particle labelled B in Fig. 3, respectively.

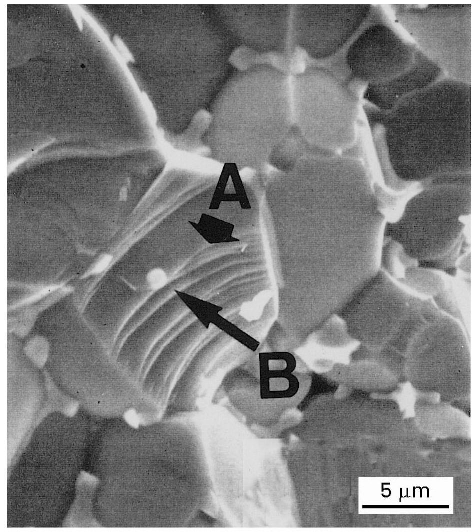

Figure 5 SEM image obtained from the fractured sample. One can see that the AlN, labelled A, is fractured in the AlN grain and the small particle labelled B, exists in the AlN grain.

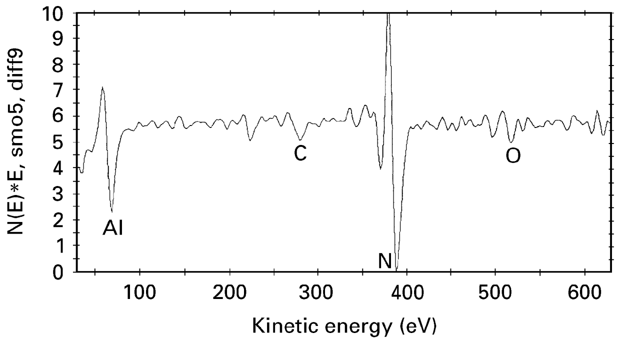

Figure 6 AES spectrum obtained from the AlN grain labelled A in Fig. 5 after etching for 3 min.

TABLE II Composition of AlN grain labelled A in Fig. 4 after etching for 3 min

Composition of the observed position (at %)					
Al	C	Ca	N	Ti	O
34	9	–	53	–	4

TABLE III Composition of the small particle, labelled B in Fig. 4 (a) before etching and (b) after etching for 3 min

	Composition of the observed position (at %)					
	Al	C	Ca	N	Ti	O
(a)	12	45	5	15	–	23
(b)	5	21	2	33	21	18

B in Fig. 5, exists in the AlN grain. Fig. 6 shows an AES spectrum obtained from the AlN grain (A) after etching for 3 min. The composition of the AlN grain is given in Table II. It is found that no calcium has dissolved into the AlN grain. Fig. 7a and b show AES spectra obtained from the small particle, labelled B in Fig. 5, before etching and after etching for 3 min, respectively. Before etching, aluminium, carbon, calcium, nitrogen and oxygen can be observed as shown in Fig. 7a. It appears that the composition of the small particle is a calcium compound such as $CaO–Al_2O_3$. After etching, however, titanium can be detected in addition to the elements observed before etching, as shown in Fig. 7b. Table III displays the composition of the small particle evaluated from AES spectra. It is found that the small particle is a titanium compound and is covered with a thin calcium compound film whose thickness is estimated to be about 5 to

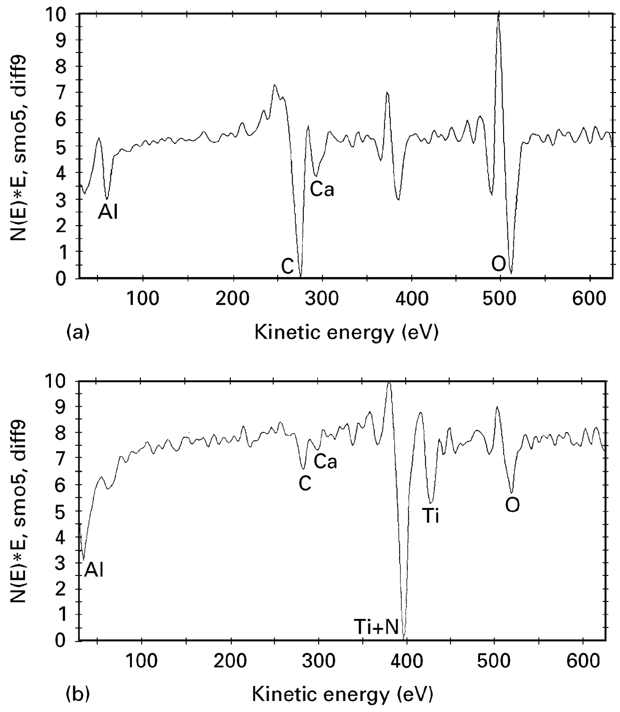

Figure 7 AES spectra obtained from the small particle labelled B in Fig. 5. (a) and (b) are obtained before etching and after etching for 3 min, respectively.

48 nm since AES can analyse about 5 nm in depth and Ar-ion etching was performed for 3 min at 16 nm min^{-1}.

It is concluded that titanium compound particles in polycrystalline AlN trap calcium since calcium can be observed only at the titanium compound particle though the concentration of calcium decreases from 0.4 to 0.004 wt % in the sintering process and calcium exists mainly at the surface of the titanium compound particle.

4. Conclusion

To clarify the role of titanium compound, i.e. as a means of calcium trapping in polycrystalline AlN, AlN–0.5 wt % TiO_2–1.5 wt % Y_2O_3-0.4 wt % CaO system was sintered at 1850 °C using a graphite furnace and the microstructure of the titanium compound particles distributed in the AlN sintered body were investigated by μ-AES.

The concentration of calcium decreases from 0.4 to 0.004 wt % after sintering. The AES studies show that the composition of the titanium compound particle is titanium, aluminium, carbon, nitrogen, oxygen and calcium. Calcium is observed at the titanium compound particle and not observed in the AlN grain and AlN/AlN grain boundary. These results indicate that the titanium compound particles trap calcium included in the polycrystalline AlN.

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