Scripta Materialia 159 (2019) 24–27

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Making insulating Al_2O_3 electrically conductive without loss of translucency using a small amount of ITO grain boundary phase

Takafumi Kusunose [a,*], Asuka Fujita [a], Tohru Sekino [b]

[a] Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, Hayashi-cho 2217-20, Takamatsu 761-0396, Japan
[b] Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

ARTICLE INFO

Article history:
Received 10 August 2018
Received in revised form 30 August 2018
Accepted 7 September 2018
Available online xxxx

Keywords:
Alumina
Indium tin oxide
Grain boundary phase
Electrical conductivity
Translucent

ABSTRACT

The electrical conductivity of Al_2O_3 must be improved from 10^{-16} S/cm to the range between 10^{-5} and 10^{0} S/cm, when insulating Al_2O_3 parts are employed for semiconductor manufacturing equipment. To remain the advantages of Al_2O_3 ceramics, it is necessary to control electrical conductivity using a small amount of conducting phase by sintering in air atmosphere. In this study, electrical conductivity of Al_2O_3 ceramics was successfully increased from 10^{-16} to 10^{-1} S/cm by precipitating a small amount of indium tin oxide (ITO) grain boundary phase, without evident deterioration of translucent of sintered Al_2O_3 polycrystals.

Al_2O_3 has excellent properties, such as high strength, high heat resistance, good plasma resistance, and low material cost [1–5]. In addition, it is characterized by low process cost that the densification can be easily attained by pressureless sintering in air. Therefore, Al_2O_3 has been one of the most widely used ceramics in structural and functional fields, such as refractory, crucible, insulator, heat sink, and substrate [6–8]. To further extend its applications for electronics and semiconductor manufacturing equipment, it is necessary to improve the conductivity of insulating Al_2O_3 from 10^{16} Ω cm to the range between 10^{0} and 10^{5} Ω cm.

In second-phase particle dispersed composites (Fig. 1(a)), contents of above 12–20 vol% are necessary for conducting particles to make insulating ceramics electrically conductive [9–12]. The addition of large amounts of second phase, however, is not desirable, because such composites might lose the excellent properties of matrix ceramics. In these electrically conductive ceramics, the press sintering methods, such as hot-press sintering and spark plasma sintering, were employed in inert gas atmosphere to fabricate sintered bodies. The press sintering method and inert gas atmosphere make their commercialization difficult. It is necessary for wide applications of Al_2O_3 ceramics in electronic fields to decrease electrical resistivity by sintering in air atmosphere without mechanically pressing.

Indium tin oxide (ITO) is well known as a transparent and conductive material. Its thin film can be produced by heat treatment in air atmosphere [13]. ITO is one of the most expected candidates of conductive second phase, because Al_2O_3 hardly reacts with indium oxide and tin oxide. However, because the shape of ITO grain is not extremely anisotropy like CNT and graphene, it is impossible to form a conducting pathway by percolation of a small amount of ITO. Hirata et al. reported that a continuous network of ITO particles as a conducting pathway was formed at 25 vol% of ITO in the Al_2O_3/ITO composites [14].

In recent years, to give electrical conductivity to insulating materials, our research group has proposed a good method that precipitates an electrically conductive material at grain boundaries (Fig. 1(b)) [15–17]. Although the volume of grain boundary phase is 1.3–3.3%, it propagates three dimensionally in a sintered body. Therefore, there is a possibility that conducting pathways in insulating Al_2O_3 is constructed by penetration of ITO liquid phase at grain boundaries between Al_2O_3 grains, because of lower melting point of ITO than Al_2O_3. Further, because the refractive index of Al_2O_3 is 1.77 that is close to 1.8–2.1 of ITO, the system of Al_2O_3–ITO might be a translucent material.

In this study, electrical conductivity of insulating Al_2O_3 was increased by pressureless sintering in air atmosphere and precipitating ITO at grain boundaries that propagated three dimensionally in a sintered body. The electrical conductivity of Al_2O_3/ITO composites was investigated by varying amounts and SnO_2 composition of ITO. In addition, the influence of a small amount of ITO on translucency of polycrystalline Al_2O_3 ceramics was evaluated.

The ITO fraction was adjusted from 0.5 to 1.5 mol%, while the weight ratio of In_2O_3 and SnO_2 was set as 100/0, 99/1, 97.5/2.5, 95/5, and 90/10 (Table 1). Commercially available Al_2O_3 powder having an average grain size of 30 nm (4 N nano alumina L30, 99.99% of purity, Anhui Junjing International Co., Ltd., Anhui, China), In_2O_3 powder having an

* Corresponding author.
E-mail address: kusuno15@eng.kagawa-u.ac.jp (T. Kusunose).

https://doi.org/10.1016/j.scriptamat.2018.09.009
1359-6462/

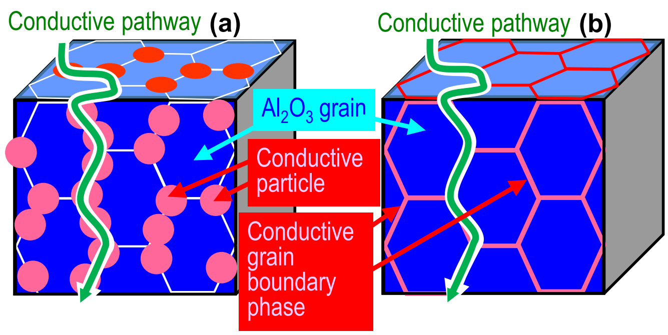

Fig. 1. Schematics of conductive pathways in insulating ceramics. (a) Dispersion of second-phase particles with electrical conductivity. The electricity flows through the second-phase particles. (b) Propagation of an electrically conductive grain boundary phase. The electricity flows through the grain boundary phase.

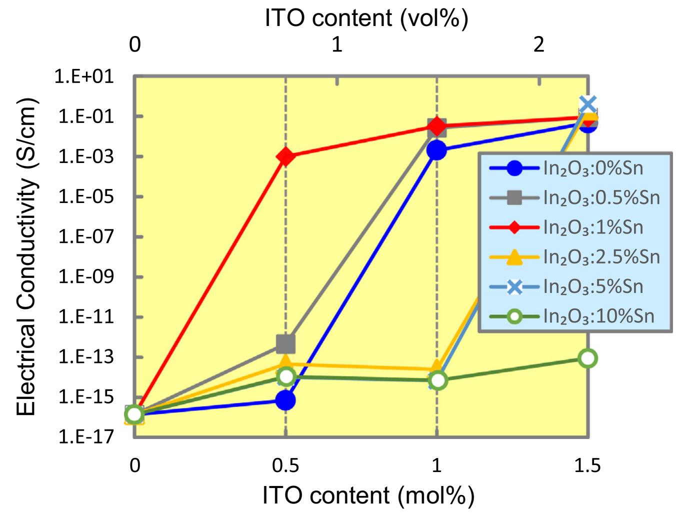

Fig. 2. Relationship between electrical conductivity of Al_2O_3/ITO composites, ITO contents, and compositions of doped SnO_2 in ITO.

average grain size of 4 μm (INO02PB, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan), and SnO_2 powder having an average grain size of 1 μm (SNO03PB, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) were mixed using an ultrasonic homogenizer to obtain homogeneously mixed powders. After drying, the mixed powder was uniaxially pressed into $\phi 15 \times 3$ mm^3 discs or $47 \times 36 \times 6$ mm^3 rectangular bars under a pressure of 10 MPa, before it was isostatically pressed at 200 MPa. The powder compacts were put on Al_2O_3 powders in an alumina crucible and sintered in air atmosphere at 1700 °C for 5 min in an air atmosphere furnace (Super Boy, Marusho Denki Co., Ltd., Hyogo, Japan). The higher sintering temperature of 1700 °C than the conventional Al_2O_3 sintering temperature of 1500 °C was adopted to form ITO liquid phase. Additionally, another commercially available Al_2O_3 powder (TM-DAR grade, 99.99% of purity, Taimei Chemical Co., Ltd., Tokyo, Japan) was also used to prepare monolithic Al_2O_3 sintered body to compare with the optical transmittance of the conventional sintered Al_2O_3.

The crystalline phases of the sintered samples were determined by an X-ray diffractometry (XRD) using Cu Kα radiation (Shimadzu Co., XRD-6100, Kyoto, Japan). The microstructure was observed using SEM (JSM-7001F, JEOL Ltd., Tokyo, Japan). The microchemical analysis of ITO grain and grain boundary phase was performed by SEM together with energy-dispersive X-ray (EDX) analysis. The electrical conductivity of the sample having conductivity of over 10^{-3} S/cm was measured at room temperature using a four-pin method resistivity meter (Loresta-GP, Mitsubishi Chemical Analytech Co., Ltd., Tokyo, Japan). The DC electrical conductivity of the samples having conductivity of less than 10^{-3} S/cm was measured using a Keithley electrometer Model 6517 controlled using a 6524-software package. Total forward transmission was measured by a double-beam spectrophotometer (V-650, JASCO International Co., Ltd., Tokyo, Japan) with a wavelength range of 200–900 nm. The sample was ground to a thickness of 0.2 mm and polished on both sides to eliminate surface scattering.

The sintered Al_2O_3 composites at 1700 °C for 5 min in air consisted of Al_2O_3 and ITO (see Fig. S1 in the Supplementary material). Fig. 2 plots the electrical conductivity of Al_2O_3/ITO composites having varying compositions and contents of ITO. The electrical conductivity increased by increasing ITO content. The Al_2O_3/1.5 mol% In_2O_3 doping 5 wt% SnO_2 (1.5 mol%-In_2O_3:5%Sn) indicated a high conductivity of 4.2 $\times 10^{-1}$ S/cm. The addition of only 0.5 mol% (0.75 vol%) of In_2O_3 doping 1 wt% SnO_2 was able to increase the conductivity to 1.0×10^{-3} S/cm. The doping of SnO_2 was more effective to enhance the conductivity than that without doping. However, the optimal doping content of SnO_2 was different for high conductivity depending on ITO content. At low contents of ITO, the doping of low wt% of SnO_2 increased the conductivity. In the Al_2O_3/1 mol% ITO, doping of 1 wt% SnO_2 increased the conductivity, which was not increased by doping of 2.5 wt% or above. On the other hand, in the Al_2O_3/1.5 mol% ITO, the conductivity increased by increasing the doping content of up to 5 wt% of SnO_2.

Fig. 3 shows the effect of doping content of SnO_2 on the shape of ITO grain boundary phase in Al_2O_3/1 mol% ITO composites. It was observed that ITO constituted grain boundary phase. Also, the EDX analysis of Al_2O_3 grains and the grain boundary phases reveal that all of trace amounts of SnO_2 was doped into In_2O_3 without any reaction with Al_2O_3. The ITO grain boundary phase was also observed at the interface of two facial boundaries in the Al_2O_3/1 mol% ITO doping 0 and 1 wt% SnO_2, whereas ITO phase was located at grain boundary triple point rather than two facial boundaries in the Al_2O_3/1 mol%-In_2O_3:10%Sn. It implies that the wettability of ITO on Al_2O_3 became poor by increasing the doping content of SnO_2. Because the poor wettability introduces difficulty to promote diffusion of grain boundary phase, it is thought that the electrical conductivity of Al_2O_3/ITO having high doping contents of SnO_2 did not increase at low ITO content. However, the high conductivities observed in Al_2O_3/ITO having high doping contents (2.5–5 wt%) of SnO_2 were obtained by increasing ITO content to 1.5 mol%.

Sintered polycrystalline Al_2O_3 ceramics have been widely used in high-pressure sodium lamps owing to its high translucency and refractoriness. Generally, it is well known that translucency of material decreases by incorporating a second phase due to phase boundary scattering arising from differences in the refractive index between matrix and the second phase. It has been reported that the high translucency of sintered Al_2O_3 remains by dispersion of a second phase, if refractive index of the second phase is similar to that of Al_2O_3 (1.77) [18].

The refractive index of ITO ranges from 2.1 to 1.8 by increasing content of SnO_2 or carrier content in ITO [19,20]. Therefore, the Al_2O_3 composite containing a small amount of ITO has a potential to be one of candidates for transparent conductive materials. Fig. 4 showed the relationship between transmittance and the amount and composition of ITO in Al_2O_3/ITO composites. The transmittance of monolithic Al_2O_3 made from L30 Al_2O_3 powder was considerably low because of high

Table 1
Compositions of ITO as a conductive phase.

Denotation	ITO composition	
	In_2O_3 (wt%)	SnO_2 (wt%)
In_2O_3:0%Sn[a]	100	0
In_2O_3:1%Sn	99	1
In_2O_3:2.5%Sn	97.5	2.5
In_2O_3:5%Sn	95	5
In_2O_3:10%Sn	90	10

[a] Monolithic Al_2O_3 made from L30 Al_2O_3 powder.