Current-Voltage Characteristics Measurements of a Grain and a Grain Boundary in SiC Ceramics Using Micro-Pattern Electrodes

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SiC セラミックスにおける微小電極を用いた結晶粒内、粒界 V-I 特性の測定

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The process and technique for direct measurement of current-voltage characteristics of a single grain boundary and a grain in silicon carbide ceramics containing beryllia were discussed. Discharging between two tips of aluminum micro-pattern electrodes by applying pulsed voltage caused melting of the tips of electrodes. As the results, aluminum-rich alloy layers were formed along the discharge path and also at the tip section of micro-pattern electrodes resulting in the breakdown of the Schottky barriers and the formation of the ohmic contacts at the interfaces of SiC and electrodes. The formation of the ohmic contacts made it possible to measure the current-voltage characteristics of a grain and a grain boundary directly.

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1. Introduction

Silicon carbide (SiC) ceramics with addition of beryllia (BeO) have been found to show a thermal conductivity of 270 W/m·K, which is higher than that of aluminum metal, and an electrical resistivity higher than $10^{13} \Omega \text{ cm}$.¹⁾ In addition, their thermal expansion coefficient is nearly the same as that of single crystalline silicon.²⁾ These remarkable properties are very suitable for semiconductor devices, especially as heat dissipation and electrical insulation substrates for LSIs and laser diodes.

A possible mechanism for the high thermal conductivity of these materials has been investigated by Ogihara et al.³⁾

They found thermal conductivity depended on the impurity concentration in the SiC grains, the low solubility level of Be into SiC grains being responsible for the high thermal conductivity. The high electrical resistivity, on the other hand, was investigated by the authors of this paper, that the unusually high electrical resistivity of these materials was caused by electrical barriers having varistor characteristics along the grain boundaries, which has been confirmed by direct

measurements of current-voltage characteristics of a single grain boundary and a grain using micro-pattern electrodes.¹⁾ However, details of the measuring process and techniques have not been reported.

In this paper the process and techniques, and also the effects of non-ohmic contacts between electrodes and SiC, are discussed.

2. Experimental procedure

2.1 Starting materials

Starting SiC materials for sintered bodies were α -type abrasive powders (GC #6000; Fujimi Kenmazai Kogyo Co.) which had an average grain size of $2 \mu\text{m}$. The powders contained nitrogen as their main electrically active impurity and they showed n -type conduction. Other impurities were as follows (wt%) : free Si, 0.68 ; free C, 0.24 ; Fe, 0.045 ; Al, 0.024 ; and SiO_2 , 0.93. Purity of BeO powder was above 99.5 wt% (reagent grade, Mitsuiwa Chemicals Co.) and its grain size was about $0.05 \mu\text{m}$ based on TEM observation.

2.2 Specimen preparation

The fabrication process of the SiC ceramics was as follows. After 2 wt% BeO powder and organic binder (e.g. a solution of polyvinyl alcohol in water or a solution of silicone resin in xylene) were added to the SiC powder, the

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composite was mixed for 0.5h in an alumina mortar and pre-pressed into green bodies of 6 mm thickness and 50 mm diameter. The green compacts had densities 53-55 % of the theoretical density. The compacts were set in a graphite die and sintered in a hot-pressing furnace at a load of 30 MPa in a vacuum of 1-10 mPa. The graphite die was heated by induction heating up to 2050°C over a 2h period and maintained at that temperature for 1h. After the furnace was cooled, the sintered bodies were taken out of the graphite die and their surfaces were ground and polished. The density of the sintered bodies was usually above 3.18 g/cm³ which was above 99 % of the theoretical density.

Micro-pattern electrodes for measuring current-voltage characteristics of a grain and a grain boundary were formed on a surface of the sintered body, the shape of which was a disc of 50 mm diameter and 2 mm thickness. After polishing into a mirror surface, the surface of the sintered body was lightly etched to reveal the grain boundaries by immersing it in a melt of Na₂O₂ and NaOH (1 : 1 weight ratio) at 400°C for 10 s. It was subsequently coated with aluminum film, 0.9 μm thickness, by a vacuum evaporation. The vapor deposited aluminum film was etched into micro-pattern electrodes (Fig. 1) by photolithography.

Two typical cases of micro-pattern electrodes were selected. In one, the tips of two electrodes were situated within the same grain and in the other, they were across a single grain boundary. The current-voltage characteristics were obtained by a curve tracer (Kikusui Densi Co., Model 583) using an intermittently applied half-wave of 50 Hz ac current.

Fig. 1. Aluminum micro-pattern electrodes formed on a lightly etched surface of the SiC sintered body by vacuum evaporation and photolithography.

3. Results and discussion

To confirm the existence of electrical barriers at grain boundaries directly, current-voltage characteristics within a grain and across a single grain boundary were measured using aluminum micro-pattern electrodes in a two terminal method. Tip sections of the micro-pattern elec-

Fig. 2. Tip sections of the micro-pattern electrodes on the SiC surface : (a) without any grain boundaries, (b) with a grain boundary between electrodes 2 and 3.

Fig. 3. Current-voltage characteristics measured with micro-electrodes shown in Fig. 2 : (a) without any grain boundaries between the electrodes corresponding to Fig. 2 (a) ; (b) with a grain boundary between the electrodes corresponding to Fig. 2 (b) (X : 5 V/div, Y : 10 μA/div).

trodes are shown in Fig. 2 corresponding to the above two cases: one with and the other without a grain boundary between the electrodes.

The current-voltage characteristics measured for the two cases are shown in Fig. 3. Both cases showed non-ohmic characteristics. However, the current-voltage curve for the case with a grain boundary between the electrodes (Fig. 3(b) measured with the electrodes 2 and 3 in Fig. 2 (b)) shifted to the higher voltage side than for the case with no grain boundary (Fig. 3 (a) measured with the electrodes 2 and 3 in Fig. 2 (a)). This result suggests that the difference in the breakdown voltage in the two cases may be caused by voltage barriers along the grain boundaries,

Fig. 4. (a) Tip sections of micro-electrodes showing discharge between electrodes 2 and 4. (b) The current-voltage relations measured with electrodes 1 and 2 (or 4) (X: 2 V/div, Y: 100 μA/div). In curve 1, current flow was from electrode 2 to 1, and in curve 2, from 1 to 2.

Fig. 5. (a) SEM micrograph observed at the tip section of the micro-electrodes in Fig. 4 (a); (b) a result of elemental analysis of Al by energy dispersive X-ray at the same area as (a).

which result from non-ohmic contacts between SiC and aluminum electrodes with the breakdown voltage of about 10 V.

To confirm this postulate, it is necessary to exclude the effects of non-ohmic contacts from the measurements. Alloys of Au-Ta and Au-Ta-Al have been reported to form ohmic contacts with n-type SiC and p-type SiC respectively.⁴⁾ However, they must be melted to make alloy layers at the interface of the electrodes and SiC, which makes it difficult, however, to get fine patterned electrodes on the SiC surface.

The SiC ceramics with addition of BeO exhibited a p-type conduction although the starting powder was an n-type semiconductor. In the sintering process, SiC grains are thought to change their conduction type from n-type to p-type by a diffusion of a small amount of Be atoms into the SiC grains, since Be works as a double acceptor in SiC. It is known that aluminum also works as an acceptor in SiC. Thus, it is anticipated that an ohmic contact can be formed if an aluminum-rich layer is formed on the SiC surface under the electrodes.

As it was difficult to use a conventional diffusion process to prepare the aluminum-rich layer for the ohmic contact, a pulse discharge method was employed. It is expected that by applying an appropriate pulse voltage between a pair of aluminum electrodes, a spark discharge may occur between the two tips of the electrodes

and cause melting at a part of the tip section of the aluminum electrodes, resulting in aluminum-rich alloy layers at the interfaces of SiC and the electrodes, and also along the discharge path.

A pulse voltage up to about 100 V was applied between a pair of electrodes, the wave-form of which was a half wave of ac 50 Hz. **Figure 4 (a)** shows an example of the discharged tip sections of the micro-electrodes. The white streak in the dark region between electrodes 2 and 4 shows the discharge path. The electrical resistance between the discharged electrodes 2 and 4 become very low and linear with the applied voltage. The current-voltage relations measured with electrodes 1 and 2 (or 4) are shown in **Fig. 4 (b)**, in which the direction of current flow was from electrode 2 to 1 in curve 1 and from 1 to 2 in curve 2. As shown in **Fig. 4 (b)**, the current-voltage relation differs according to the direction of current flow. When the current flow is from electrode 2 to 1, the current-voltage curve exhibits nearly an ohmic relation. On the other hand, the current flow in a opposite direction results in a curve of a non-ohmic relation. **Figure 5 (a)** shows a SEM micrograph observed at the tip section of the micro-electrodes in **Fig. 4 (a)**, and **Fig. 5 (b)** shows results of elemental analysis of Al by an energy dispersive X-ray method at the same area as **Fig. 5 (a)**. Electrodes numbers in **Fig. 5 (a)**, (b) correspond to those in **Fig. 4 (a)**.

From these results, it is clear that a part of the tip section of the micro-electrodes is melted and makes an aluminum-rich alloy along the discharged path, and non-ohmic contacts between electrodes and SiC were destroyed at least at the discharged tip section of the electrodes.

Figure 6 shows a model of an equivalent circuit of the non-ohmic contact and its current-voltage relation. There are two SiC-electrode interfaces. It is thought that two Schottky barriers are connected back-to-back

Fig. 6. A model of the non-ohmic contacts between aluminum electrodes and SiC: (a) an equivalent circuit; (b) its current-voltage relation.

with a grain resistor. The electrical circuit corresponding to this case is shown in **Fig. 6 (a)** and the current-voltage relation exhibits a symmetric property to the applied voltage as shown in **Fig. 6 (b)**. On the other hand when the discharge one is used as one half of a pair of electrodes, a model of the equivalent circuit is as shown in **Fig. 7 (a)** and the current-voltage characteristics exhibit a non-symmetric relation to the applied voltage (**Fig. 7 (b)**).

The current-voltage characteristics of a grain

Fig. 7. The equivalent circuit and current-voltage relation when a discharge electrode is used as one half of a pair: (a) an equivalent circuit; (b) its current-voltage relation.

Fig. 8. Tip sections of two pairs of discharge electrodes: (a) situated within the same grain; (b) situated across a single grain boundary.

Fig. 9. Current-voltage characteristics measured with micro-electrodes shown in **Fig. 8**: (a) without any grain boundaries between the electrodes corresponding to **Fig. 8 (a)** (X: 2 V/div, Y: 50 μ A/div); (b) with a grain boundary between the electrodes corresponding to **Fig. 8 (b)** (X: 5 V/div, Y: 1 μ A/div).

or a grain boundary free from non-ohmic contacts should be measured using pulse discharged electrodes. Fortunately, the pattern of electrodes used in these experiments has sets of four tip sections as shown in Fig. 1. Thus, such a set of

electrodes that had a single grain boundary or no grain boundary between two pairs of their tip sections were chosen from among the many sets of electrodes formed on the SiC surface and a pulse voltage was applied between each pair of elec-

Fig. 10. (a) SEM micrograph and (b) analysis of Al by energy dispersive X-ray of the tip section corresponding to Fig. 8 (a).

Fig. 11. (a) SEM micrograph and (b) analysis of Al by energy dispersive X-ray of the tip section corresponding to Fig. 8 (b).

trodes. **Figure 8** shows the two typical examples of the tip section of electrodes with ohmic contacts obtained by the pulse discharge method. In **Fig. 8 (a)**, the tips of the two pairs of discharge electrodes are situated within the same grain, and in **Fig. 8 (b)**, the tip pairs are situated across a single grain boundary. The results of current-voltage measurements are shown in **Figs. 9 (a)** and **(b)** corresponding to **Figs. 8 (a)** and **(b)**, respectively. When there was no grain boundary between the two pairs of discharge electrodes, the current-voltage relation exhibited nearly ohmic characteristics. On the other hand, with a grain boundary between the two pairs of discharge electrodes, varistor characteristics with a breakdown voltage of about 3-5 V were observed.

Figures 10 and **11** show SEM micrographs and results of Al analyses by energy dispersive X-ray at the tip sections corresponding to **Figs. 8 (a)** and **(b)** respectively. The aluminum-rich discharge paths on the SiC surface were not so clear as was shown in **Fig. 5**, however, a melting phenomena at the tips of the discharge Al electrodes can be observed.

As may be seen from these results, this pulse-discharge method might be very effective to have an ohmic contact between ceramic materials and metallic electrodes. However, it is difficult to know the resistivity value of a grain or a grain boundary from the current-voltage characteristics obtained here, since the strict shapes of grains or grain boundaries are unknown and thus the distribution of current flow within a grain or through a grain boundary is also unknown

although it is clear that the current flow may be restricted within a grain or through a single grain boundary when the tips of two electrodes exist on the same grain or across a grain boundary respectively.

4. Conclusions

It may be concluded that the discharging at tips of the micro-electrodes by pulsed voltage caused melting at the tips of Al electrodes, by which aluminum-rich alloy layers at the SiC-electrodes interfaces and along the discharge path between the two electrodes were formed. These layers made it possible to measure the current-voltage characteristics of a grain and a grain boundary directly without any effects of non-ohmic contacts at the interfaces of SiC and Al electrodes. Thus, this method may be very effective for destroying the non-ohmic contacts due to the Schottky barriers between ceramics and metallic electrodes.

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