Effect of B, Al, or Ga on the Piezoresistance Properties of 6H–SiC Ceramics Sintered with Carbon

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The piezoresistance coefficient was measured on SiC ceramics doped with different amounts of boron, aluminum, or gallium. The piezoresistance coefficient increased with increasing the addition within their solid solution limits. The profile of carrier concentrations, lattice constant and piezoresistance coefficient against doping levels are closely related. Only boron doped sample showed different piezoresistance coefficient and carrier concentration.

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1. Introduction

Silicon carbide ceramics have been studied as a potentially important structural ceramics and have attracted much attention as an electronic material, because they possess a wide band gap of 2–3 eV and high electric mobility.

On the other hand, semiconductor strain-sensing elements made of silicon single crystals are distinguished from other strain gauge materials by large piezoresistance coefficients or a linear increase in electric resistance in proportion to the applied tensile strain. They have therefore been applied extensively in the measurement of pressure, strain, acceleration, and force. At high temperatures, however, silicon crystal suffers from oxidation and becomes electric insulator. Consequently, it cannot be used as a stress sensor under such conditions. Therefore, oxidation resistive materials are necessary in sensor applications at high temperatures.

It has already been reported that SiC single crystals exhibit the piezoresistive effect. We have already reported a piezoresistive effect in commercial SiC ceramics fabricated by a hot press. We proposed a fracture foreseeing system that combines initial crack monitoring and bending strain monitoring utilizing the piezoresistive effect. From the preliminary experiment, we concluded that SiC ceramics has a potential to use as high temperature structural materials with a self-diagnostic function.

On the other hand, it is well known that fabrication of SiC ceramics needs high temperature or high pressure, then sintering aids such as boron/carbon (solid state sintering aid) or yttria/alumina (liquid phase sintering aid) are usually used. We have already examined the effect of a liquid phase sintering aid (yttria + alumina) on sinterability and the piezoresistive effect and also examined the effect of aluminium on the piezoresistive effect. Our previous study examined the effect of only aluminum, then it is interesting to compare the effects of the trivalent elements which are supposed to become acceptors in SiC ceramics. In the present study, we added boron, aluminum, or gallium to SiC and compared the effects on the piezoresistance properties.

2. Experimental procedure

Submicrometer-size powders of 6H–SiC (Yakushima Denko Co., Ltd., Yakushima, Japan) and boron, aluminum, or gallium (High-Purity Chemical Co., Ltd., Japan; 99.99% pure) were used as starting powders. In our preliminary experiment, only gallium added SiC powder did not attain to a favorably dense ceramics even in the maximum temperature and pressure condition in our HIP apparatus. Therefore, 1 wt% of carbon powder (High Purity Chemical, Co., Ltd., 99.99% pure) was added to any batch of powder mixtures. Powder mixtures of SiC and various amounts of trivalent metals were ball-milled in ethanol with zirconia balls for 6 hours. The relative content of doped metals in these batches was 0–1.4 wt%. As a result, molar ratio of boron to doped SiC was 0~5 mol% and those for aluminum and gallium were 0~2.1 mol% and 0~0.6 mol%, respectively. The milled slurry was dried and subsequently sieved through a 75 μm mesh. This powder was uniaxially pressed in a 10 mm die under a pressure of 30 MPa. Resultant cylindrical powder compact was followed by cold isostatic pressing under 300 MPa.

It is well known that SiC ceramics are difficult to sinter, so this study employed the hot isostatic pressing (HIP) method and 1 wt% of carbon powder as sintering aids to obtain dense specimens. The green compacts were then coated with BN powder ~5 μm thick to prevent reactions with the capsule glass during HIPing. The BN-coated specimens were put into a borosilicate glass tube to be used as the capsule. The tube was evacuated and heated to the softening temperature of the glass, then sealed and cut with a gas flame burner, closely enveloping the specimen in a glass capsule. The encapsulated specimens were HIPed under argon gas at a pressure of 195 MPa at 1950 °C for 15 min.

The theoretical density was estimated using the rule of mixtures. The bulk densities of the HIP-sintered specimens were measured by Archimedes method using deionized water as the immersion medium. The crystalline phases of the HIP-sintered SiC were analyzed by X-ray diffraction (XRD) with CuKα radiation.

The sintered bodies were cut into rectangular bars with a precision diamond cutter, and then surface polished with diamond paste (9 μm). The resulting test pieces were used to measure the effect of applied stress on the electronic resistance of SiC ceramics. The electronic resistance was measured by a two-probe direct-current (DC) method using a digital high-resistance meter (Model R8340A, Advantest Co., Ltd., Tokyo, Japan) with a constant voltage supply. Silver paste was attached to two of the parallel planes to form electrodes. These test pieces were placed on a mechanical test machine (AutoGraph AGS-5kN, Shimadzu Co., Ltd., Kyoto, Japan), and the compressive stress was increased at a constant rate perpendicular to the plane of the electrodes. During this process, the electric current change, corresponding to the
stress, was measured. From the effect of compressive stress perpendicular to the electric field on electric current change, the piezoresistance coefficient with application of perpendicular stress was calculated.

In any cases, resistance changes almost linearly with strain. The piezoresistance coefficient, $\pi$, was obtained from the following relationship between the applied strain ($\varepsilon$), Young’s modulus ($E$), and change in resistance ($R$):

$$\pi = (\Delta R / R) / (\varepsilon E)$$

The Hall Effect of SiC ceramics with various amounts of trivalent metal was evaluated using a Hall Effect evaluation system (Resitest 8300, Toyo Technica, Tokyo, Japan).

3. Results and discussion

Figures 1 (a), (b), (c) illustrate the lattice constant along the $c$ axis and the piezoresistance coefficient versus the amount of added trivalent metals up to 1 wt%. In any cases, lattice constant increases with added metals within the solution limit. The solution limits lie around 1.3 mol% in the case of aluminum, 0.2 mol% for gallium. In the case of boron doping, however, the lattice constant continues to increase up to 5 mol%.

The profiles of piezoresistance coefficient ($\pi$) closely coincide with those of lattice constants, that is, $\pi$ increases with lattice constant. In detail, $\pi$ for B doped SiC continues to increase up to 5 mol% doping and those for Al and Ga doped ones increase up to 1.3 mol% and 0.2 mol%, respectively, then level off. The $\pi$ for Ga doped sample is slightly larger than Al doped one, but both are comparable. Compared with these, $\pi$ for B doped one is much smaller while it has not been saturated in this experimental condition. Considering the covalent radii of respective atoms, B atom substitutes for carbon in SiC ceramics, while larger atoms (Al and Ga) substitute for silicon. Since only B substitutes different atom (C) in SiC ceramics, essentially different acceptor level should be formed leading to completely different piezoresistance coefficient.

Figures 2 (a), (b) and (c) illustrates carrier concentration of silicon carbide ceramics added with various amounts of (a) boron (b) aluminum and (c) gallium. The measurement of the Hall Effect indicates that any silicon carbide doped with three kind of trivalent metals are p-type semiconductors in which the carrier concentration increased with the amount added within the solution limits.

The profiles of Carrier concentration are also similar to those of lattice constant and piezoresistance coefficient. That for B doped one continues to increase and those for Al and Ga doped ones reach to saturated values. The dopant contents giving the saturation exactly coincide with those for lattice constant i.e., 1.3 mol% for aluminum doping and 0.2 mol% for gallium doping. Boron doped SiC ceramics shows small carrier concentration by one order of magnitude, which would also be derived from the unique substitution site.

We have already reported that SiC ceramics with a high acceptor concentration tend to possess a large piezoresistance coefficient.6 Such tendency was confirmed on boron and gallium doped SiC ceramics.

Conclusions

SiC ceramics doped with different amounts of boron, aluminum, or gallium were fabricated by glass capsule HIP method. Their piezoresistance properties were evaluated and following results were obtained. The piezoresistance coefficient increased with increasing the addition within their solid solution limits. The profile of carrier concentrations, lattice constant and piezoresistance coefficient against doping level are closely related. Only boron doped sample shows different piezoresistance coefficient and carrier concentration. These trivalent metals were proved to improve the piezoresistance properties in addition to facilitate the sinterability of SiC ceramics.

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Fig. 2. Carrier concentration of silicon carbide ceramics added with various amounts (a) boron (b) aluminum and (c) gallium.

References