

# Improvement of piezoresistance properties of silicon carbide ceramics through co-doping of aluminum nitride and nitrogen

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Available online 29 September 2007

## Abstract

The piezoresistance coefficient was measured on co-doped silicon carbide ceramics. Evaluation samples of  $\alpha$ -silicon carbide ceramics were first fabricated by glass capsule HIP method using powder mixture of silicon carbide and aluminum nitride with various ratios. The resultant aluminum nitride added silicon carbide ceramics were doped with nitrogen by changing the post-HIP nitrogen gas pressure. The lattice parameter increased with the amount of adding aluminum nitride indicating that the incorporated aluminum substituted smaller silicon atoms. After post-HIP treatment, lattice parameter then decreased with nitrogen gas pressure. The piezoresistive coefficient increased with the addition of aluminum nitride, it further increased with the nitrogen doping pressure.

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**Keywords:** HIP; Co-doping; Donor; Acceptor; Silicon carbide; Strain sensor

## 1. Introduction

A resistivity change accompanied by the strain of a solid is called a piezoresistivity effect, which is utilized for the direct strain sensing or stress sensing within its elastic deformation range. Silicon single crystal is almost always used as strain sensing element. This is because it has a favorable sensitivity (piezoresistivity coefficient). Furthermore, sophisticated semiconductor technologies such as processing and joining can easily be transferred.

On heating as low as 200 °C, however, its elastic deformation range becomes narrow considerably. As a result, residual strain would remain after releasing the stress needed for sensing. Another problem on high temperature operation is oxidation leading to a soar in electric resistance. In these reasons, pressure sensor available over 200 °C has not been practicably realized yet.

Silicon carbide ceramics is expecting a high temperature structural material since it has an excellent thermal durability or maintained mechanical strength at elevated temperature. Silicon carbide also attracted much attention as an electronic

material for high power devices and high temperature operation, because they possess a wide band gap of 2–3 eV. It has already been reported that silicon carbide single crystals exhibit the piezoresistive effect similar to the silicon single crystal [1]. There has been no practical application of silicon carbide single crystal for strain sensor because of its relatively small sensitivity and expensive fabrication cost.

On silicon carbide polycrystal which is advantageous for fabrication cost and mechanical strength, we have already reported a piezoresistivity coefficient comparable to that for single crystal [2–7]. Based on these data, we proposed a direct strain or pressure sensing at elevated temperature using silicon carbide ceramics of which sensitivity is barely feasible [4–6]. For sensing near room temperature, however, silicon single crystal is suitable due to its favorable sensitivity and fabrication cost. If the sensitivity of silicon carbide ceramics were enhanced to beyond that for silicon single crystal, it could substitute the strain or pressure sensing elements even near the room temperature, in addition to elevated temperature.

Compared with the exploring for a new material, it is advantageous to modify silicon carbide ceramics by incorporating variety of additives. This is because the high temperature property of silicon carbide ceramics would be maintained with the latter route. Another merit using polycrystal is a facile examination of doping effect.

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We have already examined the effect of dopant on the practically advantageous silicon carbide ceramics to improve the piezoresistive effect. The piezoresistivity coefficient is suggested to increase with increasing the doping amount within the solid solution limit in both group III and group V elements doping, e.g., 1.5 mol% in the case of aluminum [5,6,8]. We have also examined the co-doping of Al metal and atmospheric nitrogen. The effect of both dopants counteracted each other, resulting in degrading in piezoresistance coefficient [9].

In the present study, the piezoresistance coefficient was measured on co-doped silicon carbide ceramics. Evaluation samples of  $\alpha$ -silicon carbide ceramics were first fabricated by glass capsule hot isostatic pressing (HIP) method using powder mixture of silicon carbide and aluminum nitride with various ratios. The resultant aluminum nitride added silicon carbide ceramics were doped with nitrogen by changing the post-HIP nitrogen gas pressure. The piezoresistive coefficient increased with the addition of aluminum nitride, it further increased with the nitrogen doping pressure.

## 2. Experimental procedure

The  $\alpha$ -type silicon carbide powders (Yakushima Dendo Co. Ltd., Yakushima, Japan) and aluminum nitride (Tokuyama Co. Ltd., Tokyo, Japan) were mixed with a predetermined ratio (0.2, 0.4, 0.6, 0.8, 1.0, 3.0 and 5.0 wt.% of AlN). Powder mixture of SiC and AlN were ball-milled in ethanol with zirconia balls for 2 h. The milled slurry was dried and subsequently sieved through a 280  $\mu$ m mesh. About 0.7 g of this powder mixture was uniaxially pressed in a  $\varnothing$  10 mm die under a pressure of 60–100 MPa. Resultant cylindrical powder compact was packed in a polyethylene bag, followed by cold isostatic pressing under 350 MPa.

The green compacts were then coated with BN powder (GP; Denka Co., Tokyo, Japan) to prevent reactions with the capsule glass during HIP process. 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 HIP-sintered under argon gas at a pressure of 195 MPa at 1950 °C for 30 min. After breaking the capsule glass, once HIP-sintered specimens were post-HIPed at 1950 °C for 30 min under various nitrogen pressure (50–195 MPa).

The resultant sintered specimens were subjected to density measurement by Archimedes method using deionized water as the immersion medium. The crystalline phases were analyzed by X-ray diffraction (XRD) with Cu K $\alpha$  radiation.

The sintered bodies were cut into rectangular bars with a precision diamond saw (Step Cutter, Maruto Co. Ltd., Japan), and then surface polished with diamond paste (9  $\mu$ m). The resulting test pieces with dimension of 3 mm  $\times$  4 mm  $\times$  6 mm were used to estimate the applied stress dependency of electronic resistance. 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,

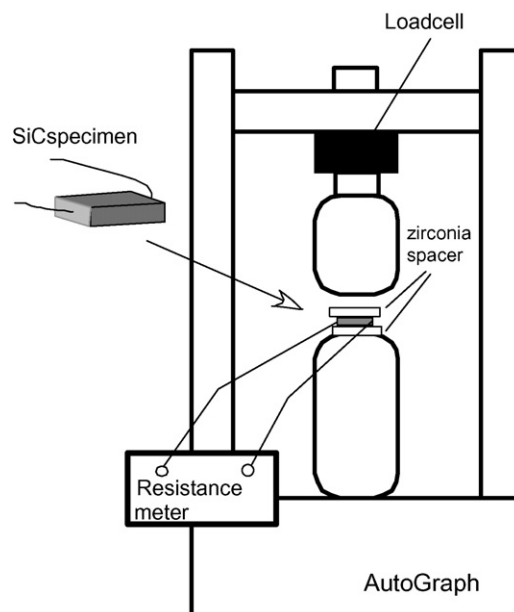


Fig. 1. Schematic set-up to measure the piezoresistivity property.

Japan) with a constant voltage supply. Silver paste was attached to two of the parallel planes (3 mm  $\times$  4 mm planes) to form electrodes. These test pieces were placed on a mechanical test machine (AutoGraph AGS-5kNG, Shimadu Co., Ltd., Kyoto, Japan), and the compressive stress was applied to the plane of 4 mm  $\times$  6 mm which was perpendicular to the plane of the electrodes, increased at a constant rate. 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 the change in electric current, the piezoresistance coefficient with application of perpendicular stress was calculated. The sample set-up is shown in Fig. 1.

In any case, resistance changes almost linearly with applied load. The piezoresistance coefficient,  $\pi$ , was obtained from the following relationship between the applied stress ( $\sigma$ ), resistance without load ( $R$ ) and change in resistance ( $\Delta R$ ).

$$\pi = \frac{(\Delta R/R)}{\sigma}$$

The Hall effects of silicon carbide ceramics with aluminum nitride and nitrogen were evaluated using a Hall effect evaluation system (Resitest 8300, Tokyo Technica Co. Ltd., Tokyo, Japan).

## 3. Results and discussion

### 3.1. Change in piezoresistive coefficient with AlN doping

First, we examined sample doped with only aluminum nitride (AlN), a group III and group IV compound. Obtained silicon carbide ceramics doped up to 5 wt.% of AlN have favorably densified with relative density over 92% of their theoretical ones. Density dependency of piezoresistance coefficient can be negligible with these samples [3].

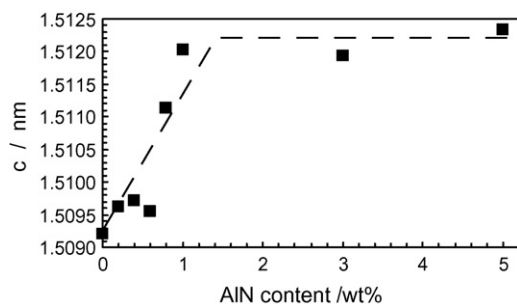


Fig. 2. Change in lattice parameter in SiC ceramics against aluminum nitride adding amount.

Fig. 2 illustrates the lattice constant along the  $c$ -axis and the piezoresistance coefficient versus the amount of added AlN up to 5 wt.%. The lattice constant increases with AlN content up to 1 wt.%, then saturated. The solution limit lies around 1.5 wt.%.

The piezoresistive coefficient measured on SiC ceramics with different amount of AlN is illustrated in Fig. 3. The piezoresistive coefficient increases with AlN content up to 1.5 wt.% then saturated. The profile of doping amount dependency of piezoresistive coefficient accords with that for lattice constant.

In order to examine the electric carrier in AlN doped SiC ceramics, Hall effects were measured. In any doping level, AlN doped SiC was proved to be n-type semiconductor. As shown in Fig. 2, the lattice constant increase with the doing amount within the solution limit. It has already reported that the impurity solution in SiC lattice is usually substitution type. Considering the covalent radii of respective atoms, Al atom (covalent radius: 0.125 nm) would substitute for Si atom (0.117 nm). Also N atom (0.074 nm) would replace C atom (0.077 nm) in the lattice. As a result, in the case of doping into SiC ceramics, the solution of Al would effect positively on lattice constant while that of N would effect negatively. The increase in lattice constant accompanied by the AlN solution would be ascribed that the positive effect of Al solution exceeds that of N solution.

In the case of AlN doping, equivalent amount of Al and N are incorporated. The electric conductivity increased with AlN amount, which would be interpreted by a larger contribution of N doping probably due to the ionization ratio and/or larger mobility of electron. This interpretation is supported by the type of semiconductor (n-type).

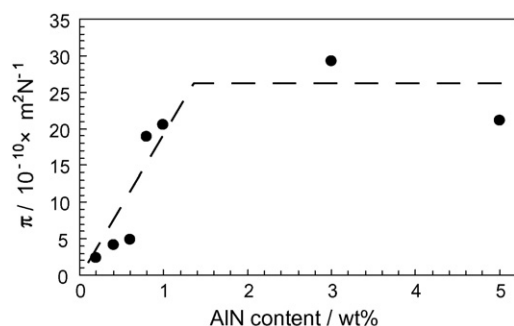


Fig. 3. Change in piezoresistive coefficient in SiC ceramics against aluminum nitride adding amount.

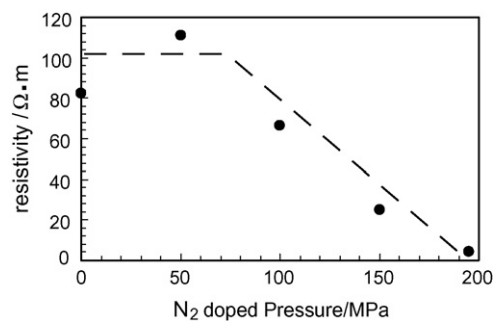


Fig. 4. Change in resistivity without load in 1 and 3 wt.% aluminum nitride doped SiC ceramics against nitrogen doping pressure.

### 3.2. Atmospheric nitrogen doping into AlN doped SiC ceramics

Fig. 4 illustrates the change in resistivity of 1 wt.% AlN doped SiC ceramics with different nitrogen doping pressure. The resistivity decreases with increasing the doping pressure. For example, it decreased to  $\rho = 4.12 / \Omega \text{m}$  after nitrogen doping with 195 MPa., which is considerably small compared with that before doping. Change in lattice parameter along  $c$ -axis are listed in Table 1 on 1 and 3 wt.% AlN doped SiC ceramics before and after nitrogen doping with 195 MPa. Lattice parameter decreases after nitrogen doping in both AlN doping levels. It can be noted that the nitrogen is incorporated into SiC ceramics even in 3 wt.% AlN doped one of which solid solution has been saturated as shown in Fig. 2.

Fig. 5 shows the piezoresistive coefficient on SiC ceramics doped with 1 or 3 wt.% of AlN followed by atmospheric nitrogen doping. The piezoresistive coefficient increases with increasing the nitrogen doping pressure both in 1 and 3 wt.% AlN doped SiC. The piezoresistive coefficient reached to

Table 1

Changes in lattice parameters ( $c$ -axis) in aluminum nitride doped silicon carbide with and without HIP treatment in nitrogen gas pressure of 195 MPa

AlN addition/HIP pressure	Lattice parameter (nm)
AlN (1 wt.%)	1.5120(5)
AlN (1 wt.%) + 195 MPa	1.5095(2)
AlN (3 wt.%)	1.5119(5)
AlN (3 wt.%) + 195 MPa	1.5083(4)

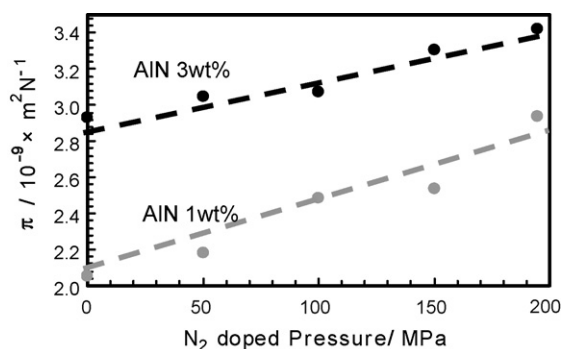


Fig. 5. Change in piezoresistive coefficient in 1 and 3 wt.% aluminum nitride doped SiC ceramics against nitrogen doping pressure.

$3.4 \times 10^{-9} \text{ m}^{-2} \text{ N}^{-1}$ , which is the maximum value reported in SiC ceramics. This enhancement in piezoresistivity would be ascribed to the further incorporation of nitrogen atom from atmosphere with high pressure into the AlN doped n-type SiC ceramics.

We have already reported that the nitrogen doping using HIP treatment degrades the piezoresistive effect in Al doped p-type SiC ceramics [9]. In the present case, however, the sensitivity or piezoresistivity coefficient increases with the same co-doping of Al and nitrogen. We have already reported that SiC ceramics with a large carrier concentration tend to possess a large piezoresistivity coefficient [5,7,8]. The electron concentration should be increased by the present two step AlN(s) + N<sub>2</sub>(g) doping, resulting in facilitating the piezoresistivity effect.

It is noted that the nitrogen solution into the SiC ceramics continued to increase up to 195 MPa post-HIP treatment in the present two step doping, while it saturated at around 150 MPa treatment in the N<sub>2</sub>(g) single step doping [8]. In the two step doping, solution amount of nitrogen should be enormous since it was incorporated into SiC as AlN(s) and N<sub>2</sub>(g). The expansion of the nitrogen solubility limit could be ascribed to the first step doping or as a result of lattice elongation by the Al doping.

#### 4. Conclusions

The piezoresistivity effect was examined on SiC ceramics doped with aluminum nitride followed by atmospheric nitrogen doping with post-HIP treatment. Without HIP treatment, AlN

doped SiC became n-type semiconductor, of which piezoresistance coefficient increased with the AlN doping amount within the solubility limits. With the post-HIP treatment, nitrogen was solved into the AlN doped SiC, leading to the enhancement of the piezoresistance property.

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