研 究

Temperature dependence of the thermoelectric properties of Si doped SiC

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SYNOPSIS

Thermoelectric properties of the Si doped SiC were measured. It is intended to reduce the thermal conductivity by addition of isoelectric element Si. Measurements of electrical resistivity, thermoelectric power and thermal conductivity were made on SiC thermoelectric semiconductor as a function of both Si doping concentration (over the range of 1.0 wt.% ~ 40.0 wt.%) and temperature (from room temperature to 750 °C). Measurements of Hall coefficient, X-ray crystallography and EPMA were also made on these samples. The thermal conductivity decreases with increase of Si concentration. At Si concentration of 40.0 wt.%, minimum thermal conductivity reached to 13 W/mK. The figure of merit Z was calculated from electrical resistivity, thermoelectric power and thermal conductivity. The maximum value of the figure of merit reaches $2 \times 10^{-4} \text{ K}^{-1}$ at 750 °C and Si concentration of 40.0 wt.%.

KEY WORDS

thermoelectric material, figure of merit, SiC

1 Introduction

Recently, strong effort has been directed towards the development of sintered thermoelectric materials^{1,2)} with improved characteristics at comparatively high temperature. The thermoelectric materials are evaluated by using the figure of merit Z . The figure of merit Z , which signifies the thermal to electrical energy conversion efficiency of the material, is defined by the following equation,

$$Z = \alpha^2 / \rho \kappa \quad (1)$$

where α , ρ and κ are thermoelectric power, electrical resistivity and thermal conductivity, respectively. One of the criterion for the practical use of the thermoelectric materials can be expressed as,

$$ZT \geq 1 \quad (2)$$

where T is the absolute temperature. It is difficult to decrease ρ and κ , and to increase α simultaneously, because α and ρ complexly depend on many parameters such as carrier concentration, carrier mobility, effective mass of carrier and etc. On the other hand, geometric factors (e. g. pores) also have effects both on ρ and κ .

Recently, SiC interests some workers as a thermoelectric material³⁻⁵⁾. SiC is a wide gap semiconductor which has enough mechanical strength and chemical stability even in the high temperature region. Therefore it is expected to use

in high temperature region. But this material has large electrical resistivity and large thermal conductivity. These properties are not favorable to increase the figure of merit. To reduce the large electrical resistivity, we have studied the thermoelectric properties of p-type SiC with doping of Al⁶⁾, Ag⁷⁾, Cu⁸⁾ and Ni⁹⁾. These dopant atoms form effective acceptor levels in SiC and the electrical resistivity is reduced drastically.

In this paper, isoelectric element Si is selected as a dopant to reduce the thermal conductivity. By the addition of Si, it is intended to introduce the scattering center of the thermal conduction.

2 Experiments

2.1 Sample Preparation

Sample preparation procedure is almost the same as described in our previous papers⁶⁻⁹⁾. β -SiC (average particle size 0.15 μm and BET surface area 19.5 m^2/g , Mitsui Toatsu Co. Ltd., MSC-20) and Si (Kojundokagaku kenkyusyo Co. Ltd., 99.99% purity) were the starting materials. Slurries were made from mixed powders of SiC and 1.0 ~ 40.0 wt.% Si powders in polyethylene jars with nylon coated steel balls as the grinding media and ethanol solution as the mixing agent. After mixing for 20 hours, the slurries were dried. The dried mixture was passed through 100 mesh sieve, granulated using 50 mesh sieve and pressed into 20 mm ϕ $\times$

6 mm pellet at $1 \times 10^7 \text{ N/m}^2$. Then the pellets were sealed into an evacuated vinyl resin tube and then pressed isostatically at $2 \times 10^8 \text{ N/m}^2$.

Each pellet was covered with the same compositional powder to prevent the compositional change during the sintering process and then placed into a carbon crucible. The sintering procedure was carried out in a furnace with a RF induction heater. It was heated up to 1000°C at a rate of 20°C/min. in vacuum, then Ar gas was introduced up to atmospheric pressure. Next the temperature was raised to the sintering temperature (2100°C) at a rate of 10°C/min. and the sample was kept at this temperature for 2 hours and cooled naturally down to room temperature. Sintered materials were cut into rectangular shaped specimens of $3 \times 4 \times 8 \sim 10 \text{ mm}^3$ in dimensions.

2.2 Sample Measurement

The crystal structure and constituent of manufactured samples were studied by using powder X-ray diffractometer and EPMA (Electron Probe Micro Analyzer).

The measurements of thermoelectric power and electrical resistivity were ranging from room temperature to around 750°C . The measurements of thermal conductivity were ranging from room temperature to around 300°C . In the calculation of the figure of merit, the thermal conductivity was assumed to be constant above 300°C .

Conventional DC method and conventional DC 4 probe method were employed for the measurements of thermoelectric power and electrical resistivity, respectively. The thermal conductivity measurement was made by a differential phase analysis of PPE (Photo Pyro Electric) method reported in our previous paper^{10,11)}.

Fig.1 The Si concentration dependence of the density and packing density of the prepared sample.

In the PPE method one can measure thermal diffusivity α_s . The thermal conductivity is given by

$$\kappa = \alpha_s \cdot d \cdot C \quad (3)$$

here, κ , α_s , d and C are thermal conductivity, thermal diffusivity, density and specific heat, respectively. We calculated specific heat of SiC/Si system from that of SiC and Si. The values of d and α_s were measured. At room temperature, we used pyro electric material PVF_2 (Poly Vinyliden diFluoride) films as heat sensor in the PPE measurement because of its high sensitivity. In the higher temperature region, we used thermocouple as mentioned in previous reports⁶⁻⁹⁾.

To clarify the carrier concentration, the Hall effects were measured by using ordinary van der Pauw method.

3 Results and Discussion

The addition of Si affects the crystalline structure of samples. The all X-ray diffraction peaks of the samples except 1.0 wt.% Si concentration were assigned to 3C-SiC (β -SiC). Only X-ray diffraction profile of the sample with 1.0 wt.% Si consists of both 3C-SiC (β -SiC) and 6H-SiC (α -SiC). At the sintering temperature of 2100°C , SiC transforms from 3C phase to 6H phase^{5,12)}. According to the previous papers⁶⁻⁹⁾, all samples doped with Al, Ag, Cu and Ni which were sintered at 2100°C show 6H phase. Addition of Si may have an effect to keep the SiC in 3C phase. No diffraction peak from Si was observed even from

Fig.2 The temperature dependence of the thermal conductivity as a function of the Si concentration measured by using PPE method. In this figure, fig.2 and fig.3, marks represent the measured points and solid lines represent the result of the polynomial which fitted to the experimental data for calculation of figure of merit.

the sample of 40.0 wt.% Si concentration. No impurities were found from analysis by EPMA.

Figure 1 shows the Si concentration dependence of the density and packing density of the sintered samples. The right side axis of the ordinates means the packing density and the left side axis of the ordinates means the sintering density. Both density and packing density decrease with increase of Si concentration especially at higher Si concentration. The sample with 40.0 wt.% Si concentration is the most porous sample in our sample preparation procedure⁶⁻⁹.

Figure 2 shows the temperature dependence of the thermal conductivity as a function of the Si concentration. All the samples show the weak decrease as temperature increases. Especially, the value of sample with 40.0 wt.% Si concentration is almost independent of temperature. At room temperature and at around 300 °C, thermal conductivity decreases with increase of Si concentration. From this figure, minimum thermal conductivity decreased to 13 W/mK. We can say that addition of Si 40.0 wt.% decreases the thermal conductivity to the one tenth of the value for the SiC prepared by the same procedure without Si. Thermal conductivity at room temperature decreases gradually with increase of Si concentration in the measured Si concentration range. On the other hand, the thermal conductivity at around 300 °C decreases steeply at lower Si concentration and decreases slowly at higher Si concentration range.

Figure 3 shows the temperature dependence of the electrical resistivity as a function of the Si concentration. The values of all samples decrease with increase of

temperature and more all samples have the similar gradient of the plots. At room temperature and at around 750 °C, the electrical resistivity shows steep decrease at lower Si concentration and decreases slowly at higher Si concentration with increase of Si concentration.

From the Hall effects measurement, hole carrier concentration is calculated up to $10^{26}/\text{m}^3$. All samples show the Hall voltage less than 40 nV under the 7 kOe magnetic field and 200 mA sample current. This large hole concentration is very close to the value of carrier concentration for metal. Since this SiC/Si system has typical semiconductor-like temperature dependence of electrical resistivity, this carrier concentration value may be too large.

Figure 4 shows the temperature dependence of the thermoelectric power as a function of the Si concentration. The all samples show the monotonous increase with increase of temperature. And more, all samples show the almost same gradients of the plots. At room temperature, the higher concentration samples show the lower thermoelectric power. On the other hand, at around 750 °C, there are no obvious relation between the thermoelectric power and the Si concentration.

Figure 5 shows the temperature dependence of the figure of merit as a function of the Si concentration. At room temperature, the samples except 1.0 wt.% and 40.0 wt.% of Si concentration show almost same value of the figure of merit. On the other hand, at around 750 °C, the figure of merit increases with increase of Si concentration.

The values of all samples increase with increase of temperature. The maximum value is reached about 2 ×

Fig. 3 The temperature dependence of the electrical resistivity as a function of the Si concentration.

Fig. 4 The temperature dependence of the thermoelectric power as a function of the Si concentration.

Fig.5 The temperature dependence of the figure of merit as a function of the Si concentration. In this figure, solid lines represent the results of calculation using the polynomials showed in the fig.2, fig.3 and fig.4. Marks are used only for identification.

10^{-4} K^{-1} at around 750°C , which is the one of the best value of the SiC based thermoelectric materials⁵⁻⁹⁾. This large Z value is achieved by reduction of the thermal conductivity and electrical resistivity. The figure of merit of the higher concentration samples (10.0 wt.%, 20.0 wt.% and 40.0 wt.%) shows linear increase with temperature. On the other hand, the figure of merit of the lower concentration samples (1.0 wt.%, 2.0 wt.% and 4.0 wt.%) shows weakly saturation tendency. Therefore we can conclude that the SiC system is a promising candidate for high temperature thermoelectric applications. It is challenging task to dope the additional impurity atoms to reduce the electrical resistivity with preserving the thermal conductivity value which is measured in this report.

4 Conclusion

The reduction of thermal conductivity is succeeded by excess addition of Si. On the other hand, electrical resistivity and thermoelectric power exhibit the anomalous behavior which is almost independent of Si concentration. The figure of merit of the sample with 40.0 wt.% Si concentration reaches about $2 \times 10^{-4} \text{ K}^{-1}$ at around 750°C , that value is very close to the criterion for practical use.

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