Thermoelectric properties of SiC thick films deposited by thermal plasma physical vapor deposition

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Received 16 December 2002; revised 16 January 2003; accepted 16 January 2003

Abstract

SiC thick films of about 300 \(\mu\)m could be prepared with a deposition rate above 300 nm/s by thermal plasma physical vapor deposition (TPPVD) using ultrafine SiC powder as a starting material. The thermoelectric properties were investigated as a function of composition and doping content. The nondoped films showed n-type conduction. Although the Seebeck coefficient reached as high as 2480 mV/K, the power factor was only around 1.6 \(\times\) 10\(^{-4}\) W m\(^{-2}\) K\(^{-2}\) at 973 K due to the relatively high electrical resistivity. In order to reduce the electrical resistivity and to deposit layers with n-type and p-type conduction, N\(_2\), B and B\(_4\)C were selected as the dopants. Nitrogen-doped samples exhibit n-type characterization, B and B\(_4\)C-doped samples exhibit p-type characterization, and the electrical resistivity decreased from 10\(^{-2}\) – 10\(^{-3}\) to 10\(^{-4}\) – 10\(^{-5}\) \(\Omega\) m after doping. The maximum power factor of the nitrogen-doped SiC and the thick films deposited with B\(_4\)C powder reached 1.0 \(\times\) 10\(^{-3}\) and 6.4 \(\times\) 10\(^{-4}\) W m\(^{-2}\) K\(^{-2}\) at 973 K, respectively.

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Keywords: Thermal plasma physical vapor deposition; Silicon carbide; Thermoelectric properties

1. Introduction

There is a growing interest in thermoelectric power generation, which allows direct conversion of thermal energy into electrical energy. Thermoelectric energy conversion has many technical advantages over other methods. For example, the devices can generate electric energy without any exhaust gases and do not contain any movable parts; therefore, no mechanical vibration and no noise are produced. Also, they are reliable for long periods without requiring maintenance. Materials such as Bi\(_2\)Te\(_3\), SiGe and FeSi\(_2\) have reached the practical application stage. However, the materials developed so far are easily oxidized, decomposed or melt above 1000 \(^\circ\)C and thus limit the efficiency of the devices. Increasing the temperature difference can improve the efficiency. Therefore, the development of high temperature thermoelectric materials is of special interest. Recent development and investigations showed that SiC and B\(_4\)C are promising candidates for high temperature applications because of their high thermoelectric power, high thermal stability, high resistance to oxidation and corrosion, and their nontoxicity [1–7].

So far, the main work on SiC as a thermoelectric material is focused on sintered SiC. However, SiC is relatively difficult to be sintered. We have successfully deposited nanostructured and thick SiC films by a novel process—thermal plasma physical vapor deposition (TPPVD), with SiC ultrafine powder as a starting material [8,9]. In this study, we report the results of thermoelectric properties of these thick SiC films.

2. Experimental procedure

The SiC thick films were deposited in a hybrid plasma processing system which has been previously described in detail [8,10–11]. Ar (55 slm) and hydrogen (4 slm) gas mixture was used as the plasma gas. Using Ar as the carrier gas, silicon carbide ultrafine powder with the average particle size of around 0.1 \(\mu\)m (Sumitomo Osaka Cement Co. Ltd) was fed into the plasma jet, completely evaporated and transported to the graphite substrate surface located 35–75 mm from the plasma torch exit. The powder feeding rate
varied from 10 to 120 mg/min. In order to control the C/Si atomic ratio of the SiC films, methane with a flow rate in the range from 0 to 500 sccm was injected as the plasma gas. The chamber pressure was maintained at a constant pressure of 250 Torr. The substrates were preheated several minutes by the plasma flame before deposition. The temperature was measured with a pyrometer.

In order to prepare films with n-type and p-type conduction and to improve the thermoelectric properties, nitrogen, B and B4C were used as the dopants. Nitrogen flow rate was in the range between 0 and 500 sccm. The purities of both B and B4C were 99%, and the average particle sizes were around 1 and 10 μm, respectively.

The deposited films were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy.

The samples for thermoelectric measurements were mechanically ground with emery paper and diamond polisher to get rid of the graphite substrate completely, and then mounted on a ceramics holder using Pt paste. The thermoelectric power, S, and the electrical resistivity, ρ, were measured in helium atmosphere using the thermoelectric power measurement apparatus ZEM-1 (ULVAC). The measurements were performed with the samples heated from room temperature to 973 K and then cooled to room temperature in steps of 50 or 100 K. Temperature differences of 20 and 40 K were applied to the two ends of the sample holder to measure the Seebeck coefficient for each temperature point. The power factor was calculated from the Seebeck coefficient and electrical resistivity.
3. Results and discussion

3.1. Preparation and structure characterization of SiC films

Fig. 1 shows the SEM fracture morphology of typical samples of nondoped, nitrogen-doped, B-doped and B₄C-doped SiC films deposited at RF power of 70 kW. The nondoped samples exhibit columnar structure, as shown in Fig. 1(a). Nitrogen doping had little influence on the cross-sectional morphology (see Fig. 1(b)). The B and B₄C additives significantly improved the dense cross-sectional morphology, as shown in Fig. 1(c) and (d), even though a layer-by-layer structure was developed for B₄C-doped films.

Fig. 2 shows the influence of the N₂ flow rate on the deposition rate with various amounts of methane injection. It can be seen that as nitrogen content in the plasma increased, the deposition rate decreased dramatically. This is due to the escape of the C source in the gaseous form of CN. The maximum thickness of the B₄C-doped dense layer reached 320 μm and a deposition rate of around 355 nm/s was achieved.

XRD analysis showed that the nondoped films deposited at <1873 K were β-SiC. When substrate temperature exceeded 1873 K, weak α-SiC peaks were detected. For nitrogen-doped samples, no Si₃N₄ peaks were detected. In the cases of B and B₄C-doped samples, however, there existed the B and the B₄C phase, respectively. EPMA analysis showed that B distribution in the surface was uniform.

3.2. Thermoelectric properties

3.2.1. Nondoped films

Fig. 3(a) shows the temperature dependence of the Seebeck coefficient $S$ of the nondoped films with that of sintered SiC, and Fig. 3(b) shows the variation of the Seebeck coefficient at around 973 K with the composition of the deposited films. The Seebeck coefficient of sintered SiC was positive, while that of all nondoped films was negative, which means that all nondoped films showed n-type conduction, while sintered SiC showed p-type conduction due to B being used as the additive during the sintering process. Temperature has little influence on the Seebeck coefficient of the films with near stoichiometric composition compared with those with composition far from stoichiometry. It can be seen from Fig. 3(b) that the film with stoichiometric composition has the largest Seebeck coefficient which reached $-480 \mu$V/K.

![Fig. 3. Dependence of Seebeck coefficient on (a) temperature and (b) composition at 973 K for nondoped SiC films.](image)

![Fig. 4. Dependence of electrical resistivity on (a) temperature and (b) composition at 973 K for nondoped SiC films.](image)
The absolute value was larger than that of the sintered SiC (361 μV/K).

**Fig. 4(a)** shows the temperature dependence of the electrical resistivity, and **Fig. 4(b)** shows the composition dependence of electrical resistivity at around 973 K. The electrical resistivity showed semiconductor-like temperature dependence. The layers with excess Si or C had lower electrical resistivity than that with stoichiometric composition (**Fig. 4(b)**), due to the increase of carrier concentration. The sample with C/Si atomic ratio of around 2.1 showed an abrupt increase of electrical resistivity. This is because, a porous film was deposited when the methane flow rate increased.

**Fig. 5(a)** shows the temperature dependence of the power factor and **Fig. 5(b)** shows the variation of the power factor as a function of composition at around 973 K. For all films, the higher the temperature, the larger the power factor. The temperature dependence is weak for the sintered SiC; it increased with increasing temperature in the range from 300 to 600 K but decreased in the range from 700 to 973 K. It is clear from **Fig. 5(b)** that the power factor showed a monotonic decrease with C/Si atomic ratio increase. This suggests that excess Si is good for improving the power factor, while excess C may be harmful for the power factor.

Although the Seebeck coefficient reached −480 μV/K, the power factor was only around 1.6 × 10⁻² W m⁻¹ K⁻² which was insufficient for practical use. This was due to the higher electrical resistivity.
3.2.2. Nitrogen-doped films

Figs. 6 and 7 show the temperature dependences of the electrical resistivity and Seebeck coefficient, respectively. All nitrogen-doped films exhibited n-type characterization. The Seebeck coefficient also decreased significantly from $2 \times 400 \mu V/K$ to $2 \times 100 \mu V/K$ after nitrogen doping. The electrical resistivity, as expected, decreased significantly from $10^{-2} \text{m}^{-1}$ for nondoped films to $10^{-4} \text{m}^{-1}$ for nitrogen-doped films, and decreased with increasing N$_2$ content in plasma, but increased with increasing CH$_4$ content. This is because, the increase of CH$_4$ content enhanced the escape of nitrogen. Both electrical resistivity and the Seebeck coefficient have weak temperature dependence. Compared with the values of the nondoped films, the power factor was significantly improved after doping, in the entire temperature range from 300 to 973 K, as shown in Fig. 8. The maximum power factor reached $1.0 \times 10^{-3} \text{Wm}^{-1} \text{K}^{-2}$ at 973 K for the sample with nitrogen doping at a nitrogen flow rate of 30 sccm. This value is comparable with those of the materials in practical use.

3.2.3. B and B$_4$C-doped films

Figs. 9 and 10 show the temperature dependence of the Seebeck coefficient and electrical resistivity, respectively, of the films with x wt% B. It can be seen that the Seebeck coefficient of all B-doped films was positive and increased with increasing B content. The electrical resistivity decreased significantly after B doping in the range of low B content ($<9$ wt%), but further increase of B content caused a dramatic increase of the electrical resistivity. This was ascribed to the formation of cracks inside the samples during mechanical grinding, because the films became crisper as B content increased.

The power factor of films with various B contents is shown in Fig. 11. As B content increased, the power factor increased, but when B content reached 12%, the power factor decreased abruptly because of the higher electrical resistivity resulting from cracks. The maximum power factor reached $1.65 \times 10^{-4} \text{Wm}^{-1} \text{K}^{-2}$ at around 973 K, which was slightly higher than that of the nondoped samples.

When B$_4$C was used as the dopant, all films exhibited p-type characteristics, as shown in Fig. 12. A Seebeck

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**Fig. 9.** Temperature dependence of Seebeck coefficient of SiC films with x wt% B additive.

**Fig. 10.** Temperature dependence of electrical resistivity of SiC films with x wt% B additive.

**Fig. 11.** Temperature dependence of power factor of SiC films with x wt% B additive.

**Fig. 12.** Seebeck coefficient of B$_4$C layer and SiC films with x wt% B$_4$C additive.
coefficients of as high as 541 μV/K was achieved for the sample doped with 3 wt% B₄C, however, it decreased with increasing B₄C content. The electrical resistivity also decreased with increasing B₄C content (see Fig. 13). Fig. 14 shows the temperature dependence of the power factor of B₄C-doped films. The B₄C film had the best power factor value among all these p-type samples, although it did not exhibit the highest Seebeck coefficient. This was because, it showed relatively low electrical resistivity.

3.2.4. Figure of merit, Z

For thermoelectric device applications, the figure of merit Z = S²/(ρ·κ), which includes the thermal conductivity of the thermoelectric material, is the decisive parameter. The thermal conductivity of films is relatively difficult to measure. Recently, Maeda et al. [12] reported that the thermal conductivity of SiC sintered at nitrogen atmosphere was around 8 W m⁻¹ K⁻¹ at 1000 K. If we take the thermal conductivity of the deposited films as 8 W m⁻¹ K⁻¹, the figure of merit, Z, of the deposited films are as listed in Table 1. For nitrogen-doped SiC films, the figure of merit at 973 K reached 0.125 × 10⁻³ K⁻¹.

| Samples                | Power factor, μ (W m⁻¹ K⁻¹) | Figure of merit, Z (10⁻³ K⁻¹) |
|------------------------|-------------------------------|------------------------------|
| Nondoped films         | 159                           | 0.020                        |
| Nitrogen-doped films   | 1000                          | 0.125                        |
| B-doped films          | 166                           | 0.021                        |
| B₄C-doped films        | 149                           | 0.019                        |

4. Conclusion

Thermoelectric properties of SiC deposited by TPPVD were investigated. TPPVD was demonstrated to be a suitable method of depositing thick SiC films using ultrafine SiC powder as a starting material. Deposition rates above 300 nm/s were achieved. The n-type and p-type characterizations of the SiC films can be simply controlled by doping with n-type dopants such as N₂ and p-type dopants such as B and B₄C. For nondoped samples, the maximum Seebeck coefficient reached ~480 μV/K, and the power factor decreased with increasing C/Si ratio. Nitrogen doping significantly reduced the electrical resistivity and thus considerably improved the power factor, even though the Seebeck coefficient was reduced. Power factors up to 1.0 × 10⁻³ W m⁻¹ K⁻² at 973 K were achieved. B-doping can also reduce the electrical resistivity, but at the expense of a severe decrease of the Seebeck coefficient. B₄C-doped films have high Seebeck coefficients, and the maximum value of 541 μV/K was achieved for 3 wt% B₄C-doped film. The film deposited from B₄C powder also showed a high power factor, 6.4 × 10⁻³ W m⁻¹ K⁻² at 973 K, due to its low electrical resistivity as well as moderate Seebeck coefficient.

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