Thermoelectric properties of boron-carbide thin film and thin film based thermoelectric device fabricated by intense-pulsed ion beam evaporation

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Abstract

Crystallized B\textsubscript{13}C\textsubscript{2} thin films were fabricated by intense pulsed-ion beam evaporation (IBE) method. Electrical conductivity and Seebeck coefficients of the obtained films were $1 \times 10^{-4}$ $\Omega^{-1}$cm and 200 $\mu$V/K at 1000 K, respectively. These values were comparable to those of bulks. For the application of the thin films, since reasonable thermoelectric (TE) properties were confirmed for the B\textsubscript{13}C\textsubscript{2} films fabricated, we attempted to develop 'in-plane' type TE device using B\textsubscript{13}C\textsubscript{2} and SrB\textsubscript{6} as p-type and n-type elements, respectively. With applying temperature difference to the fabricated device, thermo-electromotive force and electrical power were generated from the device we made, indicating that the device worked as a TE device. To the best of our knowledge, this is the first demonstration of the TE device composed of only boron-rich solids.

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1. Introduction

Many garbage-incineration facilities and power plants emit huge amount of waste heat around the environment. Recovering such waste heat as electricity is highly beneficial for carbon-dioxide reduction, saving fossil fuel, and environment protection. Since thermoelectric (TE) device can directly convert heat energy into electrical energy, the TE materials and device have been attracting considerable attention as one of the effective methods for waste heat recovery, in recent years. TE conversion efficiency increases in accordance with the dimensionless figure of merit $ZT$ defined as $ZT=\alpha^2\sigma T/\kappa$, where $\alpha$ is Seebeck coefficient, $\sigma$ is electrical conductivity, $T$ is absolute temperature, and $\kappa$ is thermal conductivity. It is, therefore, necessary to develop TE material which is stable and has large $Z$ value at high temperature.

Boron-carbide is a p-type semiconductor and stable at high temperature [1]. TE performance of boron-carbide increases even above 1000 K [2]. As a consequence, the boron-carbide is considered as an important and a promising candidate for high temperature TE conversion. Although boron-carbide has wide solid solution range, the highest melting point and highest TE performance were obtained at the composition of B\textsubscript{13}C\textsubscript{2} [3].

Making crystalline thin film of boron-carbide is very difficult because of its high melting point (2763 K). Although some attempts for realizing crystalline films have been done with pulsed laser deposition (PLD) and magnetron sputtering technique and so on, crystallized boron-carbide thin films had never been obtained without substrate heating during deposition and post annealing [4]. However, it is already reported that intense pulsed-ion beam evaporation (IBE) method enables us to deposit crystallized boron-carbide thin films without substrate heating and post annealing [5]. IBE is newly developed high-speed thin film deposition process [6,7]. High density ablation plasma...
produced by irradiation of pulsed ion-beam onto the target is solidified on the substrate and thin film with almost the same composition as that of target is formed. The B$_{13}$C$_2$ film fabricated by IBE possesses reasonable TE properties at room temperature [8].

It was already reported that strontium-hexaboride (SrB$_6$) has relatively high n-type TE properties [9]. Because of its high melting point (2600 K), SrB$_6$ is also considered as a promising high temperature TE material. Furthermore, crystallized SrB$_6$ thin films were successfully prepared by PLD, and these films showed TE properties comparable to those of bulks [10].

In this study, we prepared thin films of B$_{13}$C$_2$ by IBE and measured their TE properties at high temperature. For application of the thin film TE materials, we attempted to fabricate thin film based TE device using IBE and PLD methods. The device was fabricated by solid-state bonding technique using the B$_{13}$C$_2$ film and the SrB$_6$ film as p-type and n-type elements for the device, respectively. The open-circuit voltage and electrical power from the device fabricated were measured and the performance of the device was evaluated.

2. Experimental

Thin films of B$_{13}$C$_2$ were fabricated using intense-pulsed ion beam deposition (IBE) method. Fig. 1 shows the experimental setup of IBE method. Thin film deposition was carried out using pulsed ion beam generator (ETIGO-2). Application of 1 MV, 50 ns high and pulsed voltage to the diode induced the dielectric breakdown of flashboard attached on the anode surface, producing proton ions. High electric field between anode and cathode accelerated the ions, and ion beam was produced from the anode. Fig. 2 shows the thin film deposition process taken with high-speed camera.

Fig. 1. Schematic illustration of experimental setup for preparation of B$_{13}$C$_2$ thin films by IBE method.

Fig. 2. Thin film deposition process taken with high-speed camera: (a) ion beam bombardment onto the target, (b) plasma expansion, and (c) thin film deposition.

Thin film is deposited as following process. First, the target is bombarded with high energy density pulsed-ion beam, producing high density ablation plasma. Produced plasma expands toward a substrate which is placed facing the target, and thin film, identical to the target composition, is deposited on the substrate. Sintered B$_{13}$C$_2$ was used as a target. The sintered B$_{13}$C$_2$ target was made by the following process. The powders of boron and graphite were mixed. The powders were loaded into a graphite die, and sintered with applying a pressure of 50 MPa at 2073 K for 20 min. Quartz glass and borosilicate glass were used as substrates. During the deposition, ambient pressure and temperature were kept at 3 × 10$^{-2}$ Pa and room temperature. The distance between anode and cathode ($d_{AT}$) and that between target and substrate ($d_{TS}$) were 160 and 80 mm, respectively. Ion beam bombardment was repeated 30 times.

The targets and thin films were characterized with an X-ray diffractometer (XRD), scanning electron microscope (SEM) and energy dispersion spectrometer (EDS). The thickness of the thin films was estimated by a roughness tester. Electrical conductivity ($\sigma$) was measured by four-point probe method. Seebeck coefficient ($\alpha$) was measured by steady-state temperature gradient method.

Thin film based TE device was fabricated using SrB$_6$ and B$_{13}$C$_2$ films. SrB$_6$ film was deposited on a selected area of a quartz glass substrate through a mask by PLD method. Deposition condition for the SrB$_6$ crystalline film by PLD was reported elsewhere [10]. Subsequently, B$_{13}$C$_2$ film was deposited on the other area of the substrate, part of which overlaps with the SrB$_6$ film so as to form a p–n junction.

3. Results and discussion

3.1. Thermoelectric properties of B$_{13}$C$_2$ thin films

Fig. 3 shows the XRD spectra for B$_{13}$C$_2$ target and thin film. The spectrum indicates that the target is composed of single phase B$_{13}$C$_2$. As for the thin film, it is already confirmed that crystallized boron carbide thin films could be prepared regardless of substrate with IBE. Broad peak around 25 deg. is attributed to the borosilicate glass substrate. Obtained film was identified as B$_{13}$C$_2$ phase. From these results, it is said that single phase B$_{13}$C$_2$ thin film could be fabricated by IBE in this experiment. Thickness of the obtained film was estimated to be approximately 1 $\mu$m.
Temperature dependences of $\sigma$ for the obtained $B_{13}C_2$ film and that of bulk are shown in Fig. 4(a). Compared with the bulk $B_{13}C_2$, $\sigma$ of the film showed lower value at room temperature. The $\sigma$ was increased more rapidly with temperature, and was comparable to bulk’s value at high temperature region. Temperature dependences of $\alpha$ for the obtained $B_{13}C_2$ films and the bulk are shown in Fig. 4(b). The $\alpha$ for the obtained film is about 200 $\mu$V/K and possesses weak temperature dependence, being almost the same value and behavior as those of bulk. Although IBE method enables us to fabricate crystallized boron-carbide thin films, it is considered that certain amount of amorphous phase might be contained in the film. It was already reported that the $\sigma$ of amorphous boron-carbide is quite lower than that of crystallized one [11]. Amorphous $B_{13}C_2$ was crystallized at high temperature region, and as a result, drastic increase in $\sigma$ at high temperature was observed. On the other hand, it is known that $\alpha$ was not affected by crystallinity of boron-carbide. This appears to be the reason why no drastic change in the $\alpha$ was observed at high temperature for the boron-carbide film.

3.2. Thin film based TE conversion device composed of boron-rich solids

Thin film based TE device was fabricated using $SrB_6$ film and $B_{13}C_2$ film. Employing IBE method, which allows depositing $B_{13}C_2$ crystalline film without substrate heating, we could avoid quality deterioration of $SrB_6$ film during $B_{13}C_2$ film deposition process. Fig. 5(a) shows a photograph of the device fabricated in this study. Au films were deposited by DC-sputtering as electrodes. Thermo-electromotive force (EMF) and electrical power generated from the device were measured with applying temperature difference to the device. Measured thermo-EMF (open circuit voltage) generated from the device is shown in Fig. 5(b). The EMF increases linearly with increasing temperature difference applied to the device and reaches maximum voltage of 3.93 mV at $\Delta T = 53$ K.

The output voltage and electrical power generated from the device were measured with connecting an external load.
to the device. Fig. 6 shows the output voltage and output electrical power as a function of electric current. The output voltage decreases with increasing electrical current due to the internal resistance of the device. The maximum output electrical power of 9.15 pW could be obtained when external resistance (load) was equal to internal resistance of fabricated device. These results indicate that the fabricated device worked as a TE device. Although electrical power could be generated, the obtained electrical power was quite small. Poor σ of B$_{13}$C$_2$ film causes such low device performance. Improvement of the B$_{13}$C$_2$ film’s TE performance is necessary.

4. Conclusions

Single phase B$_{13}$C$_2$ crystalline thin films were prepared without substrate heating by IBE method. Fabricated films possessed reasonable TE properties as high as that of bulk B$_{13}$C$_2$ at high temperature, though electrical conductivity of the film was lower than bulk’s one at low temperature due to the amorphous phase existing in the film. For the application of the films, a p–n couple composed of B$_{13}$C$_2$ film and SrB$_6$ film was fabricated using IBE and PLD methods. We confirmed that the device worked as a TE conversion device. The performance of the device, however, was quite low due to mainly low electrical conductivity of the B$_{13}$C$_2$ film. To improve the performance of the device, electrical conductivity of the B$_{13}$C$_2$ film should be improved. Post annealing of the film or substrate heating during deposition so as to obtain fully crystallized B$_{13}$C$_2$ film will be one of effective ways to improve electrical conductivity of the film. And another possible way will be doping metal into the B$_{13}$C$_2$. These attempts are now in progress. Nevertheless, we succeeded in fabricating a p–n couple composed of B$_{13}$C$_2$ and CaB$_6$, which worked as a TE device. To the best of our knowledge, this is the first demonstration of a TE device composed of only boron-rich solids.

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