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Preparation and Thermoelectric Property of Boron Thin Film

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Boron thin films were deposited by electron beam evaporation and by pyrolysis of decaborane on quartz substrates. Reflection electron beam diffraction was used to characterize the crystal structure. The amorphous structure was observed for the film deposited by electron beam evaporation. The film was polycrystalline α-rhombohedral boron when the film was deposited by pyrolysis. All samples showed p-type conduction. The conductance of the film deposited by electron beam evaporation decreased linearly against T^{-4}. Linear relation was observed in the log σ against T^{-1} plot for the film deposited by pyrolysis. The thermoelectric power of the film deposited by electron beam evaporation decreased from 500 to 300 μV/K as the temperature increased from 300 to 800 K. The power factor increased from 10^{-9} to 10^{-6} $V^2\Omega^{-1}K^{-2}cm^{-1}$ with increasing temperature from 300 to 800 K. © 2000 Academic Press

INTRODUCTION

The thermoelectric converter is expected as an excellent method for energy recycling. The development of high-efficiency thermoelectric material used at high temperature is a key technology for thermoelectric energy conversion.

Boron is one of the interesting thermoelectric materials used at high temperature because of its B_{12} icosahedral structure and high melting point. Few papers have reported the electrical and thermoelectric properties of boron, since it is difficult to prepare a high-quality boron crystal (1–3).

Nakamura reported preparation and properties of amorphous boron films deposited by pyrolysis of decaborane ($B_{10}H_{14}$) (1). The thermoelectric power was about 400 μV/K at 700 K (1). Kumashiro and his co-workers reported thermoelectric properties of boron and boron phosphide (2). They reported also the thermoelectric power of about 400 μV/K for amorphous boron. The figure of merit was estimated to be higher than 10^{-5}/K at 1100 K for amorphous boron. These results suggested that boron is a promising thermoelectric material to be used at high temperature.

In this work, boron thin films were deposited by electron beam evaporation and by pyrolysis of decaborane on quartz glass substrates. The films were characterized by using reflection electron beam diffraction, XPS measurement, and thermoelectric measurement.

EXPERIMENTAL

Boron thin films were deposited by electron beam evaporation and by pyrolysis of decaborane on quartz glass substrates. Figure 1 shows the schematic diagram of the deposition apparatus.

Figure 1a shows the electron beam evaporation system. Electron beam evaporation is one of the simplest methods to form a thin film of high melting point material such as boron. The deposition chamber was evacuated by a conventional oil diffusion pump system and the pressure during evaporation was lower than 2×10^{-3} Pa. The source material was boron chip of 99.99% in purity. The substrate was heated by infrared irradiation from a carbon heater. The substrate temperature was about 300°C. Deposition was carried out for 5 min. The thickness of the film was determined from the step that appeared in the surface roughness data, and was about 500 nm.

Figure 1b shows the deposition apparatus by thermal decomposition (pyrolysis) of decaborane ($B_{10}H_{14}$). The pressure during deposition was about 5×10^{-2} Pa. The source material was decaborane of 99.9999% in purity. The decaborane is solid at room temperature and is easily sublimated slightly above room temperature. The decaborane was heated in an oil bath at 80°C. The vapor of decaborane was carried to the surface of the substrate with a nozzle made from quartz tube. The substrate was heated by an infrared lamp. This structure makes it possible to heat effectively the substrate surface where the precursors obtain the energy to form the boron film. The substrate temperature was measured by a thermocouple. The highest value was 1100°C. Boron films were deposited on the substrate surface by thermal decomposition of the decaborane. The film was deposited for about 5 min. The thickness of the film was not uniform and varied from about 250 nm at the center of the sample to less than 100 nm near the edge.

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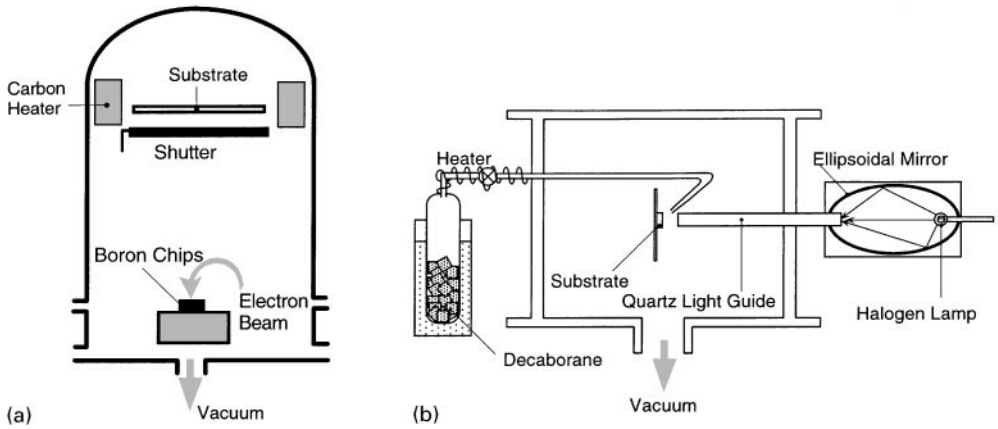

FIG. 1. Schematic diagram of the apparatus used for the deposition of boron thin films: (a) electron beam evaporation and (b) pyrolysis of decaborane.

The structure of the film was characterized by using electron beam diffraction. The chemical composition was estimated from XPS peaks. The electrical conductance was measured by using a conventional digital multimeter. Thermoelectric power was measured in a resistance furnace with temperature gradient. The electrode was formed by conductive paint. The current–voltage characteristics showed a linear relation.

RESULT AND DISCUSSION

Figure 2 shows the reflection electron beam diffraction patterns. Figure 2a shows the diffraction pattern of the film deposited by electron beam evaporation. The halo pattern with diffused rings indicated that the film was amorphous or microcrystalline. Clear rings were observed in the pattern in Fig. 2b, which was diffracted from the film deposited by pyrolysis of decaborane. The substrate temperature was 1100°C. The pattern in Fig. 2b indicated that the film was polycrystalline. The radius of the ring is consistent with the diffraction from α-rhomohedral boron.

Chemical composition was estimated from XPS measurement. In both samples, carbon and oxygen was detected as impurity. The C1s peak disappeared after ion etching for 10 min. This indicates that carbon exists only near the surface. The surface contamination seemed to be the origin of the carbon at the surface. The O1s peak was still observed after the etching. In the case of the boron film deposited by pyrolysis, the oxygen seemed to exist at the grain boundary, because well-defined spots appeared in the selected area transmission electron beam diffraction pattern (3). The spot pattern indicated that each grain consisted of α-rhombohedral boron as well as a few oxygen atoms. The same phenomena seemed to be the reason for the detection of the oxygen peak in the film deposited by electron beam evaporation, because granular structure was observed by scanning electron beam microscopy (SEM).

Electrical conductance was measured from room temperature to 900°C by a conventional digital multimeter. Figures 3 and 4 show the temperature dependence of conductance. All films showed p-type conduction. The conductance is plotted in logarithmic scale against a reciprocal temperature of $T^{-1/4}$.

Figure 3 shows the conductance of the film deposited by electron beam evaporation. The linear relation indicated hopping conduction in the film. As shown in Fig. 4, linear

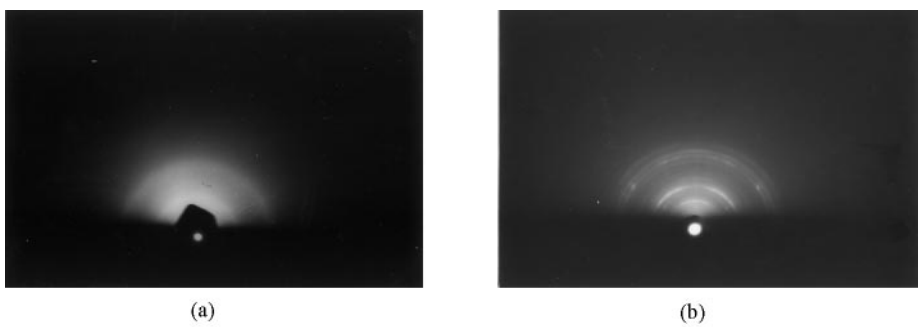

FIG. 2. Reflection electron beam diffraction patterns of boron thin film deposited by (a) electron beam evaporation and (b) pyrolysis.

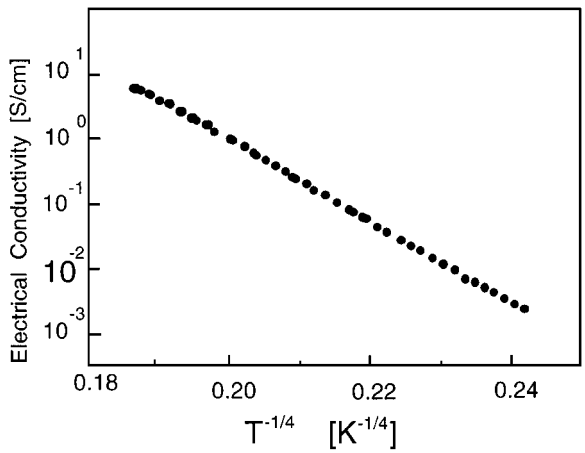

FIG. 3. Temperature dependence of the conductance of the boron thin film deposited by electron beam evaporation.

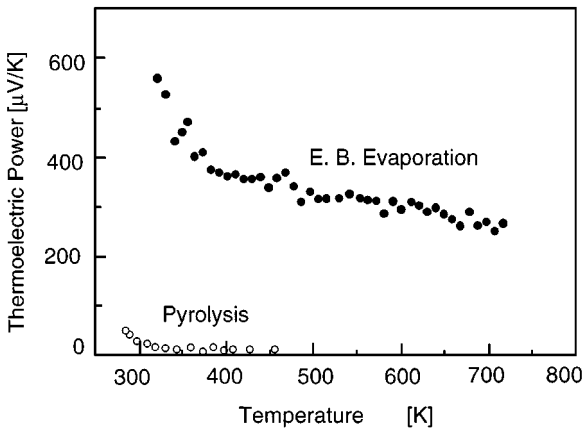

FIG. 5. Temperature dependence of thermoelectric power of boron thin films.

lines were observed in the logarithmic conductance of the film deposited by pyrolysis. The lines can be divided into three parts with different slopes. This suggests band conduction in the boron film. The activation energy of the high-temperature part was about 1.4 eV, which is consistent with the fundamental optical absorption edge of α-rhombohedral boron (4). The flat region in Fig. 4 may correspond to a saturation region, where all shallow acceptors are ionized. Low-temperature measurement is effective for showing this phenomenon, and this is now under investigation.

Thermoelectric power α was measured in a resistance furnace with a temperature gradient. The temperature difference was measured by two thermocouples attached at the sample surface. A conventional digital multimeter to measure the voltage between the hot and cold points was used.

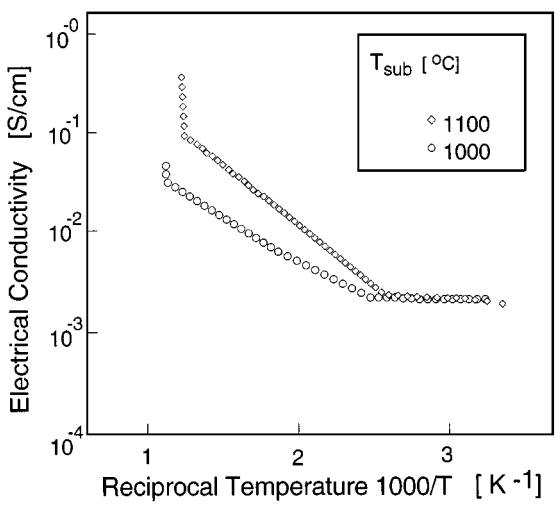

FIG. 4. Temperature dependence of the pyrolytic boron film.

Figure 5 shows the relation between the thermoelectric power and temperature. High output voltage was obtained for the film deposited by electron beam evaporation. The thermoelectric power was 300–400 μV/K in the temperature range between 500 and 800 K for the electron-beam-deposited film. On the other hand, a very low value was detected for the sample deposited by pyrolysis, although the crystallization had extremely proceeded as shown in Fig. 2. The linear relation in Fig. 4 indicates that the holes in the valence band carry the current. For the sample deposited by electron beam evaporation, evidence of hopping conduction was observed in the temperature dependence of conduction as shown in Fig. 3. This difference seemed to come from the difference in the size of periodic lattice, which can be supposed from the results shown in Fig. 2. The hopping conduction may play some roles in thermoelectric property.

Golikova *et al.* reported the thermoelectric power to be 400–650 μV/K at 400 K (5). As shown in Fig. 5, the value for the sample deposited by pyrolysis is extremely small as compared to the data by Golikoba *et al.* The reason for this difference is now under consideration.

The power factor $\alpha^2\sigma$ was estimated for the sample deposited by electron beam evaporation, where α is the thermoelectric power (Seebeck coefficient) and σ is conductivity. In Fig. 6, the power factor is plotted against temperature. The power factor increased with increasing temperature. An increase of conductance seemed to result in an increase of power factor.

In order to estimate the thermoelectric figure of merit z ($z = \alpha^2\sigma/\kappa$), the thermal conductivity κ of the material must be determined. It is very difficult to measure the thermal properties of a thin film. In this work, the value of z was estimated using the thermal conductivity reported by Kumashiro *et al.* (2) for amorphous boron wafer prepared by the CVD method. Figure 7 shows the thermoelectric

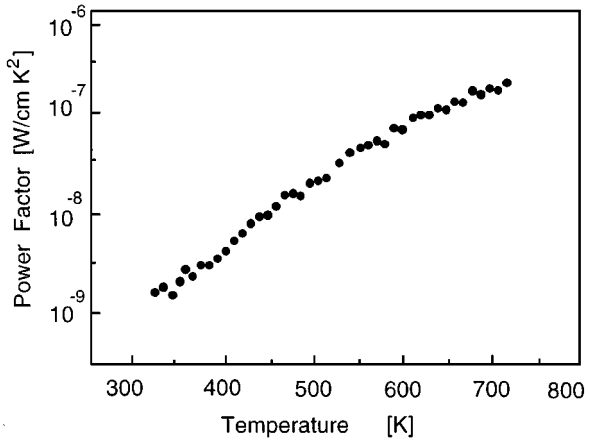

FIG. 6. Temperature dependence of the thermoelectric power factor $\alpha^2\sigma$ of the boron thin film deposited by electron beam evaporation.

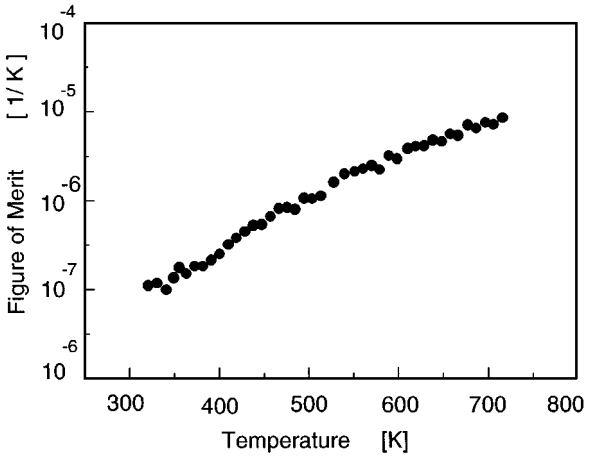

FIG. 7. Temperature dependence of thermoelectric figure of merit $z\,(=\alpha^2\sigma/\kappa)$ of the boron thin film deposited by electron beam evaporation. The value of κ is from Kumashiro *et al.* (2).

figure of merit for the boron film deposited by electron beam evaporation. The value was plotted against temperature. The figure of merit showed almost the same dependence on temperature as the data shown in Fig. 6, because the thermal conductivity was almost constant in the high-temperature region (2). The results shown in Figs. 6 and 7 suggest that the boron film may be useful for thermoelectric material used in the high-temperature range.

CONCLUSION

Boron film was prepared in order to investigate its properties as a thermoelectric material used at high temperature. Boron thin films were deposited by electron beam evaporation and by pyrolysis of decaborane. The film deposited by electron beam evaporation showed amorphous or microcrystalline structure by reflection electron beam diffraction. The film prepared by pyrolysis was polycrystalline α-rhombohedral boron. The conductance of the amorphous film showed Mott's $T^{-1/4}$ dependence. Straight lines appeared in the plots of log σ against T^{-1}. The activation energy at high temperature was consistent to the fundamental optical absorption edge of α-rhombohedral boron.

The thermoelectric power was 300–400 μV/K in the temperature range between 500 and 800 K for the electron-beam-deposited film. On the other hand, a very low value of thermoelectric power was detected for the sample deposited by pyrolysis, although the crystallization was extremely proceeded. Amorphous boron films are expected to be a promising thermoelectric material used at high temperature.

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