# Thermoelectric Properties of Boron and Boron Phosphide Films

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Amorphous boron and boron phosphide films were prepared on silica glass by a solid source molecular beam deposition (SSMBD) method and a low-pressure chemical vapor deposition method (LPCVD) by adapting gas source molecular beam deposition at a reactant pressure of 1.33 Pa. The films were characterized by X-ray diffraction, X-ray photon electron spectroscopy (XPS), and Hall effect measurements. The experimental results on film growth were correlated with the calculation by an *ab initio* molecular orbital method. The high-temperature electrical conductivity and thermoelectric power of these films were measured to evaluate the thermoelectric figure-of-merit (Z), which was determined by the electrical conductivity of the films. In particular, the Z value for SSMBD boron and LPCVD boron phosphide films was higher ($10^{-5}$/K) than those of LPCVD boron films, indicating that they are promising high-temperature thermoelectric materials. © 2000 Academic Press

## INTRODUCTION

General application of high-temperature electronic devices to wide-gap semiconductors would be promising (1). Boron-based semiconductors are refractory semiconductors and high thermoelectric powers for a high-efficiency direct energy conversion. Previously we prepared *p*-type amorphous and polycrystalline boron and *n*-type polycrystalline boron phosphide wafers by a conventional thermal chemical vapor deposition (CVD) process at 1 atm and measured electrical, thermal, and thermoelectric properties of these specimens up to 1000 K. The figure-of-merit (Z) of a polycrystalline BP wafer is $10^{-7}$/K at high temperatures while that of an amorphous boron is $10^{-5}$/K (2).

The present paper has evaluated thermoelectric properties of PVD boron and boron phosphide films prepared on an insulating substrate as well as solid source molecular beam deposition (SSMBD) (3) and low-pressure CVD (LPCVD) processes with the aim of integrating the thermoelectric device. The films including substrates have many complicated parameters, such as stress and Piezo effects and a thermal diffusion, so the evaluation was performed by simplifying the factors with respect to the substrate. As a result we have confirmed the highest thermoelectric power

ever known. In addition, the species in the gas phase of diborane are examined on the basis of a quantum chemical calculation and *in situ* mass spectroscopic analysis (4).

## EXPERIMENTAL

Experimental conditions for the preparation of films are summarized in Table 1. We have prepared boron and boron phosphide films on silica glass substrates by SSMBD (4) and LPCVD methods.

Boron crystal ($> 6N$) used in SSMBD was supplied by Tokuyama Corporation. Boron evaporated by an electron beam gun (3 kW) at an emission current of 100 mA was supplied on the substrate maintained at the condition from room temperature to 800°C at the pressure of $1.33 \times 10^{-4}$ Pa.

We applied a gas source molecular beam deposition (GSMBD) at a molecular flow region (5) to operate a viscous flow region of 1.33 Pa, which is referred to as LPCVD in the present experiment. Then the flow rates of diborane for 20–50 sccm (standard cubic centimeters per minute) and of phosphine for 50 sccm were used to increase incident frequencies of reactant gases. The reactant gases of diborane (2% in hydrogen) and phosphine (20% in $H_2$ and 100%) were introduced into the chamber through variable leak valves. A growth temperature of 700°C for boron and boron phosphide films was chosen in reference to the GSMBD process (5) with nearly the same growth rates. Boron films were produced by $B_2H_6$ cracked at 300°C under a pressure of 1.33 Pa for the deposition time of 8 h, where the substrate temperature above 500°C is necessary to desorb hydrogen from the growth surface. The boron films were deposited on silica glass substrates at gas flow rates of 20–50 sccm for diborane. Diborane (2% in $H_2$) cracked at 300°C and phosphine (20% in $H_2$ and 100%) cracked at 900°C were used to grow boron phosphide films on a silica glass substrate for 10 h.

The crystal structure of the films was studied by X-ray diffraction (XRD) techniques. The composition of boron phosphide films were determined by X-ray photoelectron spectroscopy (XPS). Ohmic contacts of the films were made by evaporated Al or Au followed by annealing in argon at

**TABLE 1**
**Experimental Conditions for Film Growth**

| Method | Substrate temperature | Raw materials | Flux intensity | Cracked temperature (°C) | Growth time | Reactant pressure (Pa) |
|---|---|---|---|---|---|---|
| SSMBD | RT–800°C | B solid crystal (> 6 N) | $1.0 \times 10^{18}$ atoms/min | — | 40 min | $1.33 \times 10^{-4}$ |
| LPCVD | 700°C | $B_2H_6$ (2% in $H_2$) | 20–50 sccm | 300 | 8 h | > 1.33 |
| LPCVD | 700°C | $B_2H_6$ (2% in $H_2$) | 20–50 sccm | 300 | 10 h | > 1.33 |
| (for boron phosphide) | | /$PH_3$ (20% in $H_2$ and 100%) | 50 sscm | 900 | | |

400°C for 1 h. Electrical properties of the specimen at room temperature were measured by the van der Pauw method. A block diagram of the apparatus for the thermoelectric measurement is found in Refs. (5, 6). An electrical conductivity of the films was measured by a two-terminal method at temperatures between room temperature and 800°C under argon atmosphere. Thermoelectric voltage between hot and cold junctions was measured under a constant temperature gradient of 2–3°C.

## RESULTS AND DISCUSSION

### A. Film Preparation and Characteristics

All films show an amorphous structure determined by a XRD as shown in Fig. 1. Since XRD measurements were performed on the films with a silica glass, the broad peaks near 22° would reflect those of silica glass. Boron and boron phosphide should show peaks near 22° and 35°, respectively. The peak at 22° for boron films would overlap with that of a silica glass so no difference is observed between them. The structures of the films are amorphous, so they have many structural defects, but the correlation with electrical properties is not clear. The sign of thermoelectric voltage between hot and cold junctions and the measurements of a Hall effect indicate that they are all p-type conductors. Temperature dependence of the deposition rate for SSMBD boron films is shown in Fig. 2, which is different from that for a GSMBD film (5). The growth rate in a GSMBD process is determined by an incident frequency of the raw material when there is an enough energy to absorb, while the evaporation condition by an electron beam is constant. Thus the growth rate becomes constant above 400°C. Hydrogen desorption has to be performed for both LPCVD and GSMBD boron films while it is not necessary for SSMBD boron films. Then a low activation energy for the SSMBD boron of 9.17 kJ/mol is observed in comparison with that for the GSMBD method, 168 kJ/mol (5), and that for the LPCVD method.

The SSMBD films have a resistivity of $10^2$–$10^3 \Omega \cdot$cm, a carrier concentration of $\sim 10^{14}$/cm³, and a mobility 0.2–0.8 cm²/V·s depending on the substrate temperature. Figure 3 shows the growth temperature dependencies of the carrier concentration, the mobility, and the resistivity. Except for room temperature growth, the hole concentration decreases and the hole mobility increases with a rise in growth temperature from 200 to 800°C, resulting in a slight increase in resistivity. The film prepared at room temperature has a high resistivity, which would be due to a high concentration of structural disorders in comparison with
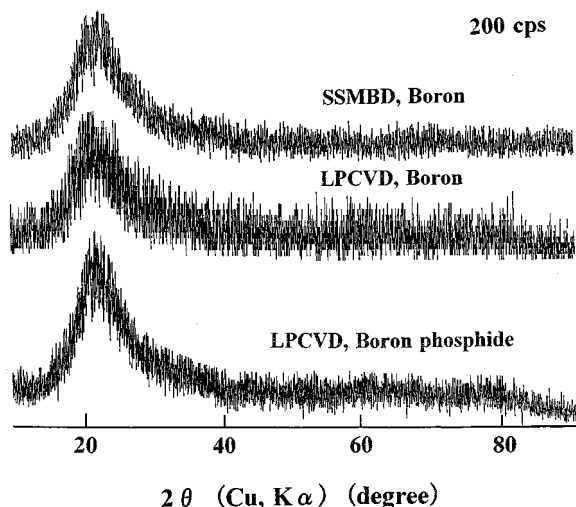


**FIG. 1.** XRD of SSMBD boron and LPCVD boron and boron phosphide films on silica glass.
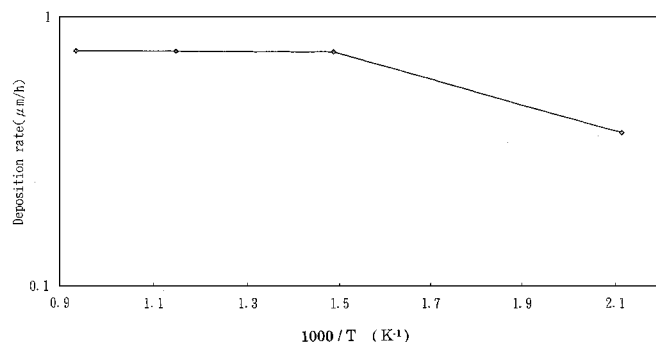


**FIG. 2.** Relationship between growth rates and reciprocal temperatures for SSMBD boron films.
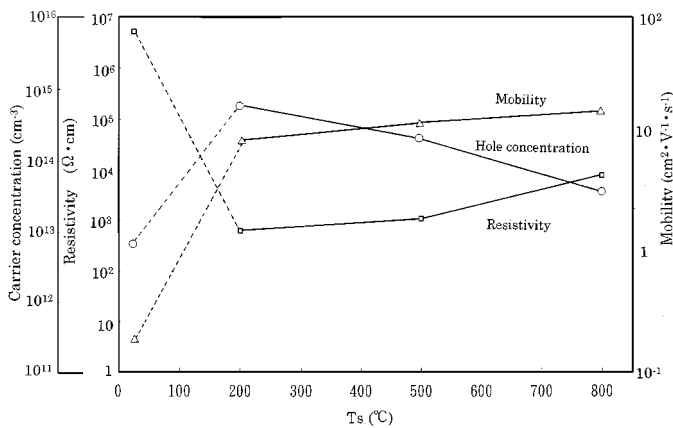
**FIG. 3.** Growth temperature dependencies of (○) hole concentration, (△) mobility, and (□) resistivity for SSMBD boron films.

other films. No noticeable difference in the XRD pattern is observed, but the electrical properties are improved with the rise in growth temperature. As is mentioned later, a low electrical resistivity contributes to a high thermoelectric figure-of-merit.

The present LPCVD boron and boron phosphide films give the growth rate of 0.2 μm/h, which is higher than the GSMBD films (5). The GSMBD has been performed in the molecular flow region(5), but the present LPCVD corresponds to a viscous region, which produces a high growth rate due to an increase in incident frequencies of the reactant gases. The surface of the substrate was first considered to be terminated with hydrogen. In the course of film growth, hydrogen was desorbed and precursors would stick to the hydrogen-desorbed sites as in the case of the surface processes in a silane plasma CVD (7). Whether thermal desorption of hydrogen occurs or not is determined by the growth temperature. If the desorbed sites were covered with enough precursors, film growth would not occur. In the case where the substrate temperature was fixed, the number of absorbed sites was also constant. Then film growth was determined by hydrogen desorption so the dependence of growth rate on the gas flow rate would become constant, giving of 0.2 μm/h.

Mass spectroscopic analysis revealed that the concentrations of $B_3H_x$ ($x = 0$–3) were high at the optimum conditions for boron deposition (4). They were considered to be the main precursors of icosahedral boron films. They can be produced by gas-phase reactions of $BH_x$ and $B_2H_x$. Stable structures and relative stabilities of $B_3H_x$ ($x = 0$–3) were quantum chemically determined by using an *ab initio* molecular orbital method (4). In the case of $B_3H_x$ ($x = 0$–3), triangular forms, which are the basic unit of the icosahedral structure, are more stable than linear forms. Stable $B_2H_4$ structures produced by cleavage of terminal hydrogens from $B_2H_6$ were discovered. $BH_x$ were considered to be produced

by cleavage of the center B–H–B bond of $B_2H_6$. The activation energy of the most favorable primary decomposition mode ($B_2H_6 \rightarrow 2BH_3$) was calculated to be 2.4 eV. Then a self-aggregation process calculated by an *ab initio* orbital method is summarized as follows:

$$B_2H_6 \rightarrow BH_{x(x=0-3)}, B_2H_{x(x=0-4)} \rightarrow B_3H_{x(x=0-3)} \rightarrow B_{12}H_x.$$
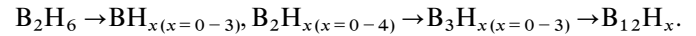
In this way main precursors produced by association reactions of products of a primary decomposition of diborane in LPCVD were determined by the combination of theoretical and experimental studies.

A boron phosphide film was deposited by involving the simultaneous presence of both boron precursors $B_3H_x$ ($x = 0$–3) and phosphorus precursors $PH_x$ ($x = 0$–3) and $P_2$ on the substrate at high temperatures 600–700°C where deposition rate is determined by boron flux (5). The incident phosphorus atoms could absorb onto the growing surface to form a migration state so that P atoms would be incorporated into the crystal. The incorporation probability is controlled by the effective concentration of P atoms in the migration state. The composition of the boron phosphide film by XPS (Fig. 4) is 77:23 B:P. This is consistent with the calculation by an *ab initio* molecular orbital method where diborane tends to self-aggregate to form $B_3Hx$ to make a boron cluster in the boron phosphide film. It should be noted that the phosphorus contents of the boron phosphide films are not influenced by the $PH_3:H_2$ ratio from 20 to 100%. Boron–boron bonds are easily formed by self-aggregation. On the other hand, phosphorus–phosphorus bonds are not easily formed. This is considered to be a reason why films are boron-rich.

Figure 4 shows the XPS (XSAM-800 Shimadzu-Kratos) spectra of LPCVD boron and boron phosphide films. The peaks at bonding energies of 130.5, 188.3, 288.0, and 512.0 eV correspond to phosphorus $2p$, boron $1s$, carbon $1s$, and oxygen $1s$, respectively. The amounts of carbon and oxygen at the surface were estimated from the observed peak intensities multiplied by the empirically derived atomic sensitivity factors for XPS (B, 0.13; P, 0.39; C, 0.25; O, 0.66) indicated that C:B and O:B are 0.09 and 0.04, respectively. Oxygen decreases a little by Ar ion etching, even though the apparent carbon content decreases. It is difficult to remove oxygen from the film surface by Ar ion etching. The oxygen atoms are incorporated into the films during the film growth process due to a high base pressure in the chamber and a low film growth rate.

The electrical conductivity of LPCVD films is lower than that of SSMBD films by two orders of magnitude. The LPCVD films do not contain hydrogen, but trap levels would be formed by the hydrogen desorption during film growth, which produces a low electrical conductivity.

The LPCVD boron films have a high resistivity due to many structural disorders so we could not obtain good
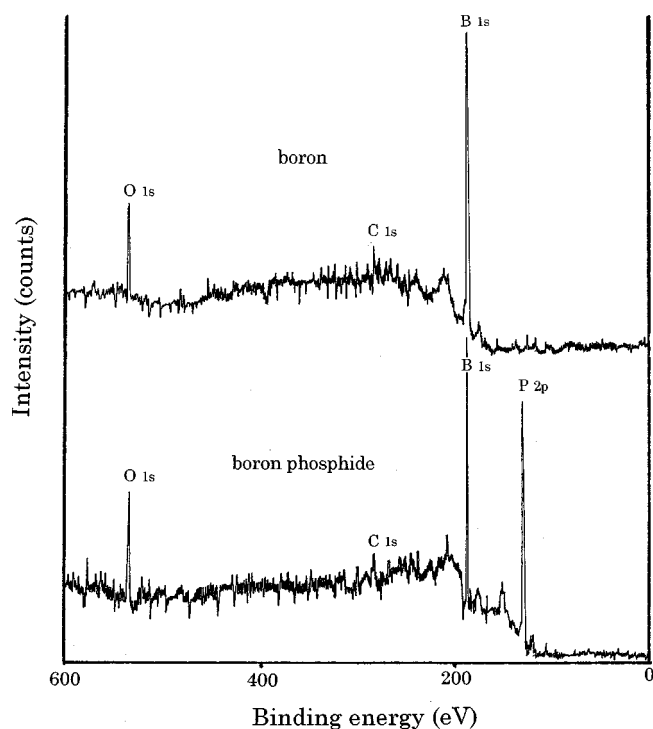
**FIG. 4.** XPS spectra of LPCVD boron and boron phosphide films.

ohmic contact, which makes it impossible to measure a Hall effect at room temperature by the van der Pauw method. In the case of boron phosphide films two types of species, i.e., boron and phosphorus, would stick to desorbed hydrogen sites on the surface of the substrate, while in the case of boron only boron species would stick to the growing film, producing many structural disorders. Then we restrict the data for LPCVD boron phosphide in a Hall effect measurement.

The results of Hall effect measurements of boron phosphide films are shown in Fig. 5. $p$-type conductors correspond

to boron-rich boron phosphide. A LPCVD boron phosphide film has the highest mobility and the lowest hole concentration at the diborane flow rate of 40 sccm under a constant phosphine flow rate of 50 sccm. The minimum defect concentration would occur in the equilibrium condition between absorption and desorption rates for the reactant gases on the substrate. Then there might exist an optimum gas flow rate for boron phosphide. A high mobility film has a low hole concentration and a high electrical conductivity. A low carrier concentration and a high electrical conductivity would be due to a low defect density.

These films display an amorphous structure, but a band conduction would be applicable considering the mobility (Fig. 6).

### B. Thermoelectric Properties

We have measured the thermoelectric properties of SSMBD boron and LPCVD boron and boron phosphide films prepared under various growth conditions mentioned Section A. The best results are obtained for the following experimental conditions: SSMBD boron growth temperature of 500°C; LPCVD boron flow rate of $B_2H_6$ 40 sccm; LPCVD boron phosphide flow rate of $B_2H_6$ 40 sccm under $PH_3$ 50 sccm.

Temperature dependencies of the electrical conductivity ($\sigma$) for SSMBD boron and boron phosphide films are shown in Fig. 7. We could measure $\sigma$ of boron phosphide at higher temperatures than for boron, which would be caused by low stress from the silica substrate. Boron films are destroyed at 800 K by thermal stress while boron phosphide films are stable up to 1000 K. A match of thermomechanical properties, such as a thermal expansion coefficient and elastic moduli between the film and a silica glass would be better for boron (8).
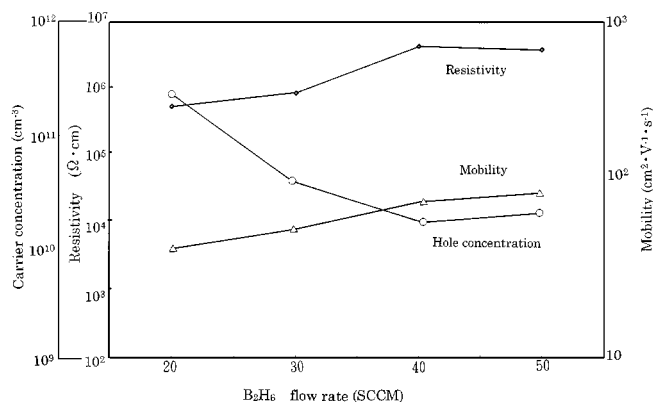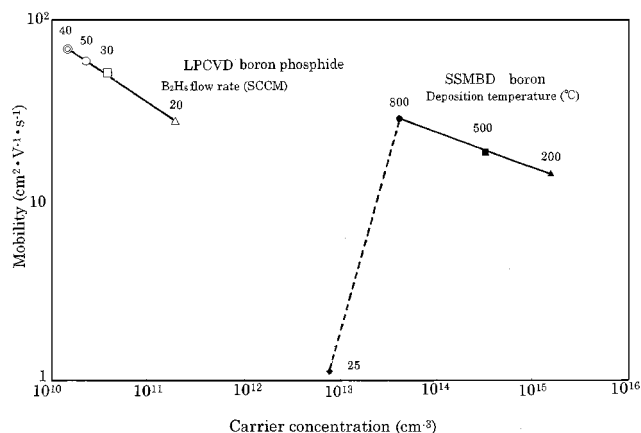


**FIG. 5.** Results of Hall effect measurement in LPCVD boron phosphide films as a function of $B_2H_6$ flow rate under constant $PH_3$ flow of 50 (sccm).



**FIG. 6.** Relationship between mobility and carrier concentration for SSMBD boron films and LPCVD boron phosphide films.
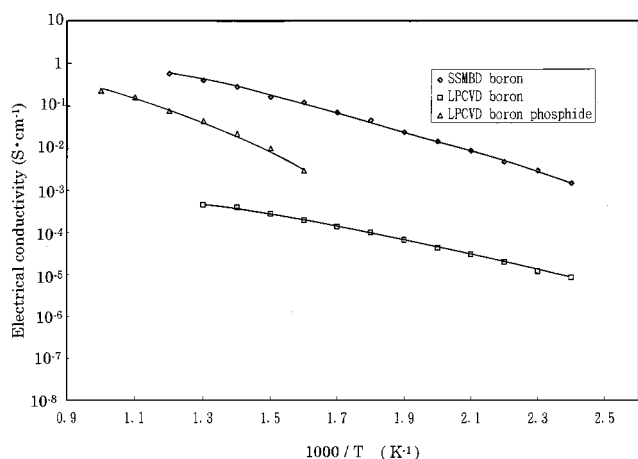
**FIG. 7.** Temperature dependencies of electrical conductivities ($\sigma$) for boron and boron phosphide films.

The present films have high resistivity so it is necessary to measure thermoelectric properties above 400–600 K. The differences in the electrical conductivities between SSMBD and LPCVD films would reflect the concentrations of trap levels due to the hydrogen desorption reaction in the film growth process.

Hydrogen desorption does not exist in a reaction for SSMBD boron films so a trap level due to hydrogen desorption is not formed. The trap density for LPCVD boron phosphide films would be reduced when the phosphorus atoms are terminated at the growth surface after hydrogen desorption. Then SSMBD boron and LPCVD boron phosphide films show high electrical conductivity in comparison with LPCVD boron films. The LPCVD boron film has too high a resistivity to measure a Hall effect at room temperature, which would be due to the formation of many trap levels by hydrogen desorption during film growth. Although plots of log $\sigma$ versus $T^{-1/4}$ and log $\sigma$ versus $T^{-1}$ show a good linear relation over a wide range of temperature, we do not believe that this proves a hopping conduction. Temperature dependence of the electrical conductivity shows a band conduction with activation energies of 1.19 eV for SSMBD boron film and 0.825 eV for LPCVD boron films. Then trap densities for the SSMBD films are lower than those for LPCVD boron and boron phosphide films.

Electrical conduction in boron-based compounds is a very complex process, characterized by superposition of a high-mobility microscopic band-type conduction and a low-mobility hopping drift (9). The results depend on the method of preparation and measurement. In the case of an amorphous boron wafer (5) with a low mobility of $10^{-2}$ to $10^{-3}$ cm$^2$/V·s, the relationship between log $\sigma$ and $1/T$ is slightly concave, but that between log $\sigma$ and $T^{-1/4}$ is linear, explained by hopping conduction. The conductivity of the crystalline boron wafer with a mobility of 1.1 cm$^2$/V·s shows a gradual increase up to 800 K, above which it increases steeply, beyond which it increases steeply with temperature with an activation energy of 1.5–1.6 eV, being nearly the bandgap of an $\alpha$-rombohedral boron (1.9 eV). The intrinsic conduction begins to appear at a high temperature, so that a thermally activated band conduction would be applicable. On the other hand, the dielectric function in the frequency range $10^4$–$10^9$ Hz for the interpretation of the transport mechanism in a boron carbide can be fitted neither by a hopping process nor by band-type conduction alone. An excellent fit is obtained when a superposition of a both mechanisms is assumed (9). Then, it is difficult to determine the conduction mechanism by the temperature dependence of electrical conductivity only.

The temperature dependence of the electrical conductivity for boron phosphide films can be understood as a competition between the decrease in mobility and the increase in carrier concentration as was observed for single-crystalline wafers (10). The temperature dependence of the electrical conductivity ($\sigma$) has a thermal activation energy of 1.34 eV. The phosphorus in the boron phosphide films would reduce the impurity level. At room temperature the conductivity is low, because most of the carriers are frozen out on the acceptor centers. As the temperature rises, the degree of ionization of acceptors increases, and the rising carrier concentration results in a rapid increase in the electrical conductivity. At around 770–1000 K depending on the specimens, the conductivity tends to saturate, because of compensation of ionized acceptors. At a considerably high temperature, a very steep rise in conductivity should occur, due to the onset of an appreciable intrinsic conduction, which is not confirmed in the present study.

The temperature dependencies of the thermoelectric power ($\alpha$) of boron and boron phosphide films are shown in Fig. 8. These amorphous films show unusual behavior: an almost constant or gradual increase in thermoelectric power for the entire temperature range. A high thermoelectric power is consistent with the high resistivity of the films. The large value of the thermoelectric power and the increase with increasing temperature were predicted by Emin (11) and Aselage (12) for a polaron hopping system in which disorder is present in the hopping sites. Emin also proposed a phonon-drag effect (13). However, the present thermoelectric power of the films on a silica glass has extremely high values of $\sim 1$ mV/K, and increases with increasing temperature, which differs from that of films grown on a sapphire single crystal (14). Matsubara (15) confirmed an anomalously high thermoelectric power of $\sim 5$ mV/K for amorphous Fe$_{1-x}$Cr$_x$Si$_2$:O films with a $p$-type conductor on a silica glass grown by an ionized-cluster beam method, indicating that Si–O would be an important factor to determine a high thermoelectric power. The high-temperature growth would result in Si–O bonds in the film which would be expected to
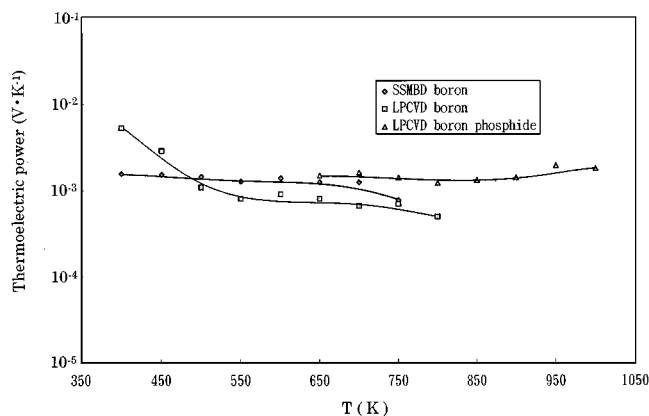
**FIG. 8.** Temperature dependencies of thermoelectric power ($\alpha$) for boron and boron phosphide films.

by the electrical conductivity where an increase in electrical conductivity produces a high $Z$. High $Z$ values are obtained at 400–800 K for the SSMBD boron film and at 800–1000 K for the LPCVD boron phosphide film, which would be due to good adhesion between boron phosphide film and silica glass. The electrical properties of the film are influenced by the substrate at high temperatures, so the matching of thermomechanical properties between film and substrate is a very important factor. In the present case the boron phosphide film would represent a good match between them and would be less influenced by the substrate than the boron film.

## CONCLUSION

We have prepared boron and boron phosphide films with amorphous structures by SSMBD and LPCVD methods. The experimental results on the preparation of films are consistent with the calculation by an *ab initio* molecular orbital method that diborane tends to self-aggregate to form $B_3H_x$ incorporated into boron clusters in the film. SSMBD and LPCVD boron films have activation energies for electrical conduction of 1.19 and 0.825 eV, respectively, while LPCVD boron phosphide film has an activation energy of 1.34 eV. LPCVD films would form the trap levels by hydrogen desorption during film growth so they have a lower electrical conductivity than SSMBD films. However, the present films are characterized by an intrinsic high thermoelectric power of $\sim 1$ mV/K. Thus the thermoelectric figure-of-merit for these films depends on electrical conductivity, where the increase in electrical conductivity produces a high figure-of-merit. High $Z$ values are obtained at 400–800 K for the SSMBD boron and at 800–100 K for the LPCVD boron phosphide.

produce a high thermoelectric power. The thermoelectric power of the present films is not dependent on the preparation method and condition, showing intrinsic high values of $\sim 1$ mV/K.

The thermal conductivity ($\kappa$) of the present films with 1-$\mu$m thickness on silica glass would be determined by the thickness of the silica glass, 300 $\mu$m. Then thermoelectric figures-of-merit $Z = \sigma\alpha^2/\kappa$ are calculated by measuring the thermal conductivity of the silica glass by a laser flash method. $Z$ values for the present films are shown in Fig. 9. SSMBD boron films have high electrical conductivity so the highest $Z$ value of $\sim 10^{-4}$/K is obtained. But LPCVD boron films have a low $Z$ values because of low electrical conductivity. The LPCVD boron phosphide film with a high mobility has a high $Z$ value. The maximum $Z$ for boron phosphide is $1.7 \times 10^{-5}$, which is higher than that for the CVD wafer (2). The figure-of-merit would be determined
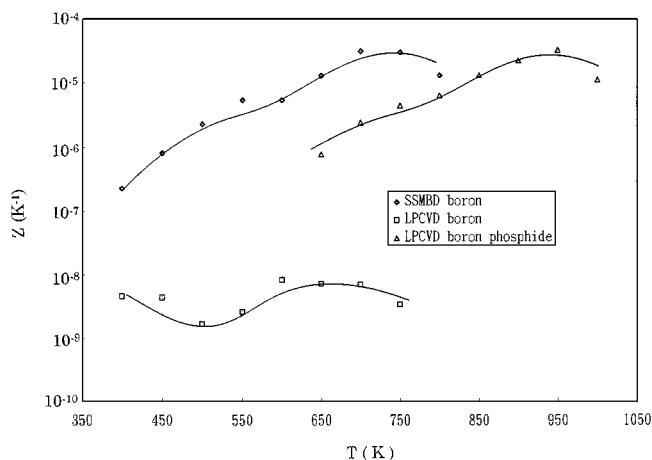
**FIG. 9.** Temperature dependencies of thermoelectric figure-of-merit ($Z$) for boron and boron phosphide films.

## REFERENCES

1. H. Werheit, *Mater. Sci. Eng. B* **29**, 228 (1995).
2. Y. Kumashiro, T. Yokohama, A. Sato, and Y. Ando, *J. Solid State Chem.* **133**, 314 (1997).
3. Y. Kumashiro, T. Yokoyama, J. Nakamura, and J. Takahashi, *Jpn. J. Appl. Phys.* **10**, 168 (1994).
4. K. Sato, N. Kanda, T. Ogata, and Y. Kumashiro, *Chem. Phys. Lett.*, in press (2000).
5. Y. Kumashiro, T. Yokoyama, T. Sakamoto, and T. Fujita, *J. Solid State Chem.* **133**, 269 (1997).
6. K. Nakamura, *J. Electrochem. Soc.* **131**, 2691 (1984).

7. A. Matsuda and K. Tanaka, *J. Appl. Phys.* **60,** 2351 (1986).

8. K. Kamimura, M. Ohkubo, T. Shionomiya, M. Nakano, and Y. Onuma, *J. Solid State Chem.* **133,** 100 (1997).

9. H. Werheit, A. Hausen, and H. Binnenbrunck, *J. Phys. Condens. Mater* **8,** 7263 (1996).

10. Y. Kumashiro, M. Hirabayashi, and T. Koshiro, *J. Less-Common Met.* **143,** 159 (1988).

11. D. Emin, *Phys. Rev. Lett.* **35,** 882 (1995).

12. T. L. Aselage, *Mater. Res. Soc. Symp.* **234,** 145 (1991).

13. D. Emin, *AIP Conf. Proc.* **140,** 189 (1985).

14. Y. Kumashiro, T. Yokoyama, J. Nakamura, K. Matsuda, and J. Takahashi, *Mater. Res. Soc. Symp.* **242,** 629 (1992).

15. K. Matsubara, Science and Techology for Energy Conversion (Sub-arec), p. 32 (1990).