

Thermoelectric properties of photo- and thermal CVD boron and boron phosphide films

Y. Kumashiro,* T. Enomoto, K. Sato, Y. Abe, K. Hirata, and T. Yokoyama

Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Received 27 September 2002; received in revised form 6 May 2003; accepted 12 May 2003

Abstract

The electrical properties of n-BP films newly prepared by thermal CVD in the B_2H_6 – PH_3 – H_2 system were improved by a deuterium lamp excitation. High-temperature electrical conductivity and thermoelectric power of amorphous boron and polycrystalline boron phosphide films grown on silica glass were measured to evaluate the thermoelectric figure-of-merit (Z). In particular, the Z -value for photo-thermal BP films was higher ($10^{-4}/K$) than that of boron films, indicating that they are promising for high-temperature thermoelectric materials.

© 2003 Elsevier Inc. All rights reserved.

Keywords: Amorphous boron films; Polycrystalline boron phosphide films; van der Pauw method; Electrical conductivity; Thermoelectric power; Thermoelectric figure-of-merit

1. Introduction

Boron and boron compound semiconductors have high thermoelectric power, which make them applicable for high-temperature thermoelectric devices [1]. Previously we have calculated first excitation energies, oscillator strength, and potential energy surfaces of B_2H_6 and PH_3 by using an ab initio molecular orbital method and prepared p-type boron and boron phosphide films by the photo-thermal CVD process using B_2H_6 – PH_3 – H_2 systems [2]. As a result, deuterium lamp irradiation is effective for the excitation of both B_2H_6 and PH_3 in photo- and thermal chemical vapor deposition (CVD) to grow boron and boron phosphide films at 600–1000°C [2]. The electrical properties of p-type boron and boron phosphide films on silica glass were improved by deuterium lamp irradiation. Now we have succeeded in preparing n-type boron phosphide films by the same method through the reduction of B_2H_6 gas flow rates from 20 to 4 cm³/min under the same PH_3 and H_2 gas flow rates.

The present paper summarizes the thermoelectric properties of boron and boron phosphide films by photo-thermal and thermal CVD processes.

2. Experimental

The reaction gases B_2H_6 (1% in hydrogen) and PH_3 (5% in hydrogen) were used in a CVD furnace, equipped with a deuterium lamp for optical excitation [2]. After heat treatment of substrate [3], the two source gases were mixed with hydrogen at the growth temperature. An n-type BP was prepared at gas flow rates of 4, 500, and 2500 cm³/min for diborane, phosphine, and hydrogen, respectively, in the temperature range 600–900°C at a deposition time of 2 h with and without the deuterium lamp excitation. The films were characterized by X-ray diffraction (XRD). Evaporated Ag, followed by annealing in argon at 400°C, made ohmic contacts of the films. A linear relationship between I (μA) and V (mV) was observed in the ranges 1–1000 μA and 0.3–500 mV obeying the ohmic law. Electrical properties of the films at room temperature were measured by the van der Pauw method.

Electrical conductivity of the films was measured by a two-probe method at temperatures between room temperature and 800°C under an argon atmosphere [3]. Thermoelectric voltage was measured in a resistance furnace with a temperature gradient of 2–3°C [4]. The temperature difference was measured by two thermocouples attached at the film surface. A conventional

*Corresponding author. Fax: +81-45-339-3949.

E-mail address: kumashiro@ynu.ac.jp (Y. Kumashiro).

digital multimeter was used in order to measure the voltage between the hot and cold points.

3. Results and discussion

3.1. n-Type boron phosphide films

The XRD of photo-thermal CVD n-BP on Si (100) oriented predominately on (100), while that of the thermal one showed various orientations. The crystal distortion of photo-thermal n-BP films is less than that of thermal ones. The tendency is almost the same as that of p-type BP [2]. The XRD of n-BP films on silica glass grown above 700°C shows a distorted polycrystalline structure, but that of films grown below 650°C shows amorphous structure. Strong diffractions from BP (200) and BP (400) planes are observed for photo-thermal CVD films grown above 700°C. Crystal distortion of the photo-thermal CVD films is less than that of the thermal films and that of n-type film is similar to that of p-type film [2].

The n-type BP films grown at 600°C contain many strong structural disorders and a high resistivity due to a low growth temperature, so we could not obtain good ohmic contact, which makes it impossible to measure the Hall effect at room temperature by the van der Pauw method. The electrical properties of the present n-type boron phosphide films on silica glass grown above 700°C with and without optical excitation by a deuterium lamp are shown in Fig. 1. The growth temperature dependences of the crystallinities and electrical properties of p-type films [2] are similar to those of n-type films. n-Type doping of boron phosphide film is due to excess phosphorus [5]. Photo-thermal n-type CVD boron phosphide tends to have higher mobility and lower carrier concentrations than thermal CVD ones as was shown in p-type boron phosphide [2].

The supply of B_2H_6 gas to the reactant chamber in n-type BP is less than that of p-type ones because the

flow rates of B_2H_6 for n-type growth are one-fifth that for the p-type one, so hydrogen and phosphor content in the reactant chamber increase. Then n-type BP would contain much trap due to the hydrogen desorption reaction [4] in the film growth. The trap density for n-BP would be higher than that for p-type ones, resulting in a lower carrier concentration in n-type than p-type.

3.2. Thermoelectric properties

The electrical conductivity (σ) for the amorphous boron film increases exponentially with increasing temperature (Fig. 2). Each curve is composed of two straight-line segments of different slopes corresponding to different activation energies. The conductivity of photo-thermal CVD borons (Fig. 2) was higher than those of thermal CVD ones, indicating improvement of the short-range order of the film. The activation energies for the extrinsic region are 0.11 eV for photo-thermal CVD and 0.16 eV for thermal CVD films. The activation energies at high temperatures are 0.84 eV for both CVD processes, being near the band gap of amorphous boron of ~ 1.0 eV [6,7]. The curve of photo-thermal CVD boron (Fig. 2) in the X-axis between 1.2 and 1.4 would

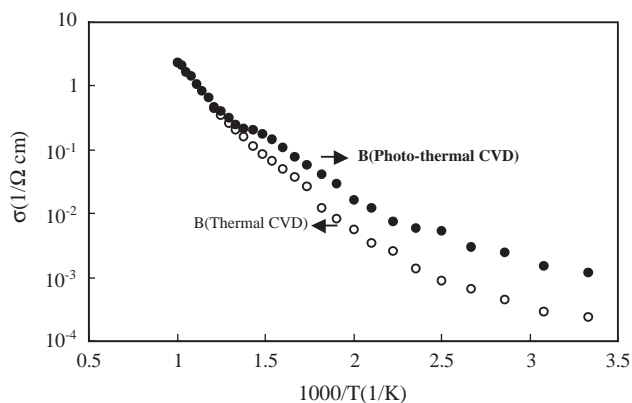


Fig. 2. Temperature dependence of electrical conductivity of amorphous boron films.

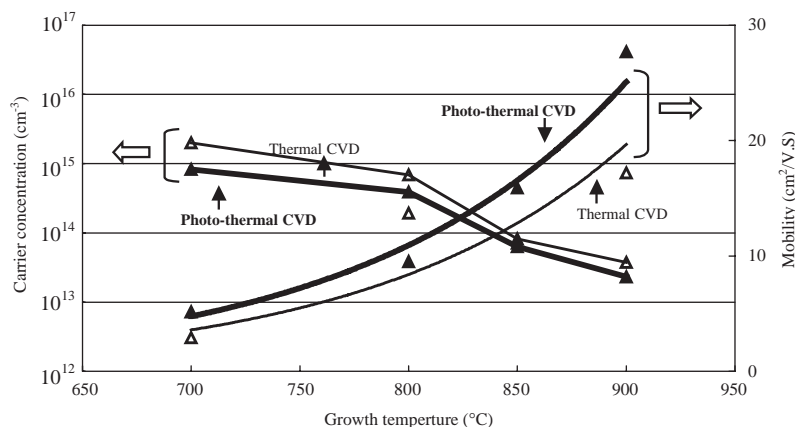


Fig. 1. Electrical properties of n-type boron phosphide films grown on silica glass at various growth temperatures.

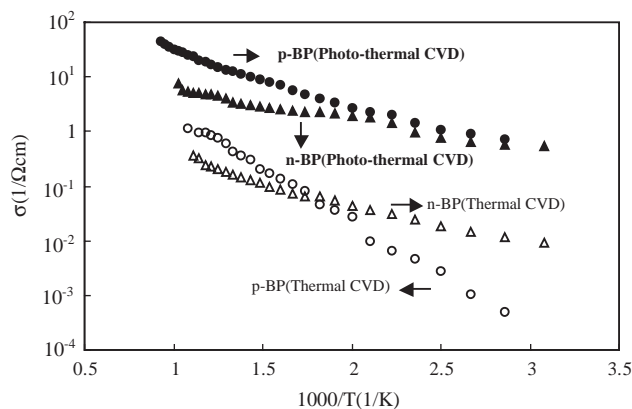


Fig. 3. Temperature dependence of electrical conductivity of polycrystalline boron phosphide films.

be a saturation region owing to complete ionization of the acceptors. Details of this were not clarified because the measurement of conductivity at increasing and decreasing temperatures respectively ended in failure due to the destruction of films.

Temperature dependence of the electrical conductivities for polycrystalline BP films (Fig. 3) indicates that decomposition of reactant gases by the deuterium lamp irradiation would reduce the defect concentrations in the films increasing the electrical conductivities. The activation energy of 0.10 eV for photo-thermal n-BP and 0.13 eV for thermal ones at low temperatures would be caused by doubly charged phosphorus (P^{2+}) [5]. Our previous work [5] indicated that the activation energies associated with acceptor levels were 0.2 and 0.32 eV. Then the activation energies of p-BP are 0.17 eV for photo-thermal and 0.33 eV for thermal CVDs, due to the formation of impurity states. Low carrier concentrations at high temperatures with an activation energy of 1.9 eV in p-BP would correspond to intrinsic conduction ($E_g = 2.1$ eV), while 1.5 eV in n-type was not in the intrinsic range but the transition region from saturation to intrinsic ones. The activation energy for conductivity in the impurity region is lower for photo-thermal CVD films in comparison with thermal ones, which would indicate the effect of decomposition and excitation of B_2H_6 and PH_3 by the deuterium lamp irradiation [2].

The temperature dependencies of thermoelectric power (α) for these films are shown in Fig. 4. An anomalously high thermoelectric power of ~ 5 mV/K for amorphous $Fe_{1-x}CrSi_2O$ films on silica glass indicates that Si–O would be an important factor to determine a high thermoelectric power [8]. The high-temperature growth would result in Si–O bonds in the film, which would be expected to produce a high thermoelectric power. Then high thermoelectric power would be due to Si–O bonds in the films [4,8].

Amorphous boron films show unusual behavior: increases with increasing temperature for thermal

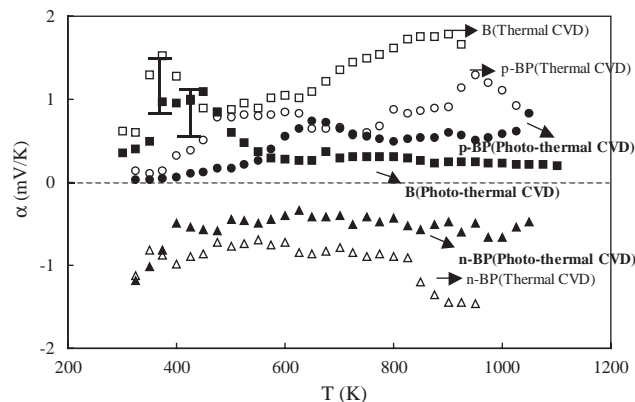


Fig. 4. Temperature dependence of thermoelectric power of boron and boron phosphide films.

CVD boron and maximum values at lower temperature ranges or a small peak in thermoelectric power. The absolute thermoelectric power for boron phosphide films is almost constant, gradually increases, or gradually decreases. The absolute thermoelectric power for thermal n-type CVD BP film tends to increase above ~ 800 K, indicating that electron concentration ranges in the impurity region and Fermi energy is lowered by electron supply from the donor level with increasing temperature [9]. The absolute thermoelectric power of photo-thermal CVD films tends to be lower than that of thermal ones. Especially a remarkable decrease in α for photo-thermal CVD boron film should be noted. However some exceptions are observed for p-BP between 600 and 700 K and for B between 300 and 500 K, which would probably be caused by a stress effect [10] or piezoresistance characteristics [11]. Thermoelectric power is also related to disorder states in the specimen. An increase of thermoelectric power for p-type films would be explained by an additional term representing the entropy associated with the transport of vibration energy with carriers [12]. The photo-thermal CVD film has less disorder than thermal ones, reducing absolute thermoelectric power.

It is very difficult to measure the thermal conductivity of a film. The thermal conductivity (κ) of the present films with several μm thickness on silica glass, 300 μm , would be determined by that of the silica glass [4]. The estimated thermoelectric figure-of-merit ($Z = \alpha^2 \sigma / \kappa$) [4] is calculated by measuring the thermal conductivity of the silica glass by a laser flash method.

Z-values for the present films are shown in Figs. 5 and 6. Z-values for photo-thermal CVD boron film increase with the increase of temperature and saturate above 800 K. That for the thermal one is lower than the photo-thermal one at intermediate temperature ranges and reaches $10^{-4}/K$ above 800 K. High Z-values are obtained at 500–1000 K for photo-thermal CVD boron and at 800–1000 K for thermal CVD boron. Z-values

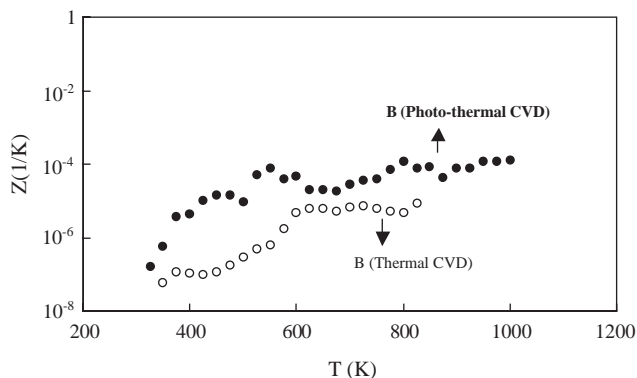


Fig. 5. Temperature dependence of thermoelectric figure-of-merit of amorphous boron films.

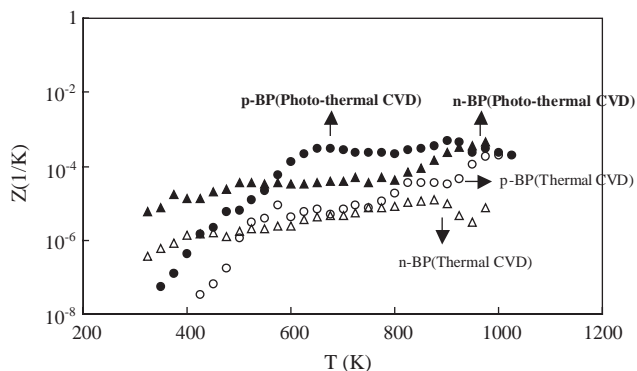


Fig. 6. Temperature dependence of thermoelectric figure-of-merit of polycrystalline boron phosphide films.

for BP films tend to increase with temperature, but photo-thermal BP had higher Z -value than the thermal one. Especially photo-thermal n-BP has high Z -values of $10^{-4}/\text{K}$ at high temperatures and p-type BP has $10^{-4}/\text{K}$ above 600 K. Photo-thermal BP films are promising for thermoelectric materials at high temperature. The figure-of-merit in the present films would be characterized by the high electrical conductivity.

4. Conclusion

We have measured the thermoelectric power for photo-thermal and thermal CVD boron and boron

phosphide films deposited on silica glass in the $\text{B}_2\text{H}_6\text{-PH}_3\text{-H}_2$ system. The present films are characterized by an intrinsic high thermoelectric power of $\sim 1 \text{ mV}/\text{K}$. The thermoelectric figure-of-merit of these films depends on electrical conductivity, where the increase in the electrical conductivity produces a high figure-of-merit. High Z -values are obtained at 500–1000 K for photo-thermal CVD boron and at 800–1000 K for thermal CVD boron. Photo-thermal BP films have high Z -values of $\sim 10^{-4}/\text{K}$ at high temperature.

Acknowledgments

This work was supported by the Foundation for Promotion of Material Science and Technology of Japan (MST Foundation).

References

- [1] H. Werheit, *Mater. Sci. Eng. B29* (1995) 228–232.
- [2] Y. Kumashiro, K. Sato, S. Chiba, S. Yamada, D. Tanaka, K. Hyodo, T. Yokoyama, K. Hirata, *J. Solid State Chem.* 154 (2000) 39–44.
- [3] Y. Kumashiro, Y. Okada, H. Okumura, *J. Cryst. Growth* 132 (1993) 611–613.
- [4] Y. Kumashiro, K. Hirata, K. Sato, T. Yokoyama, T. Aisu, T. Ikeda, M. Minaguchi, *J. Solid State Chem.* 154 (2000) 26–32.
- [5] Y. Kumashiro, M. Hirabayashi, T. Koshiro, *J. Less-Common Metals* 143 (1989) 159–165.
- [6] H.O. Pierson, A.W. Mullendore, *Thin Solid Films* 63 (1979) 257–261.
- [7] K. Nakamura, *J. Electrochem. Soc.* 131 (1984) 2691–2697.
- [8] K. Matsubara, *Science and Technology for Energy Conversion, Subarec*, 1990, p.32.
- [9] S. Yugo, T. Kimura, *Phys. Stat. Sol. (a)* 59 (1980) 363–370.
- [10] Y. Kumashiro, T. Yokoyama, A. Sato, Y. Ando, *J. Solid State Chem.* 133 (1997) 314–321.
- [11] K. Kamimura, M. Ohkubo, T. Shinomiya, M. Nakano, Y. Onuma, *J. Solid State Chem.* 133 (1997) 100–103.
- [12] T.L. Aselage, *Mater. Res. Soc. Symp. Proc.* 234 (1991) 145–156.