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The properties of B–Sb thin films prepared by molecular flow region PVD process

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Abstract

The present paper is the first description on the electrical and thermoelectric properties of amorphous PVD $B_{12}Sb_2$ films prepared using the reaction of decaborane gas with evaporated antimony gas on Si (1900 Å) / SiO_x (3700 Å) / Si (100) (625 μm) substrate at the temperature 350°C. Ohmic metals contacts of the film were examined by making evaporated Al, followed by annealing at 200°C. The comparatively high mobility of $\sim 100\,cm^2/V\,s$ and high thermoelectric figures-of-merit of $\sim 10^{-4}/K$ were confirmed.

Keywords: $B_{12}Sb_2$ film; Molecular flow region PVD process; van der Pauw method; Electrical conductivity; Thermal diffusivity; Thermoelectric power; Thermoelectric figure-of-merit

1. Introduction

Antimony (Sb) based III–IV compound semiconductors were paid much attention as advanced device application due to high mobilities.

We have been studying boron-based semiconductor films [1] to evaluate new electronic materials. If we could prepare a boron antimonide (BSb) film, enhanced mobility would be expected to produce new electric materials.

We proposed newly designed BSb based on band calculation [2] by Ferhat et al. and succeeded in preparing $B_{12}Sb_2$ film on Si (100) plane at temperatures 200–400°C by molecular flow (MF) region PVD process for the first time [3].

The present paper describes electrical properties by Hall effect at room temperature and thermoelectric properties up to high temperatures.

2. Experimental

We used a vacuum evaporation chamber to operate the molecular flow region CVD (MFPVD) process [3] using decomposed decaborane ($B_{10}H_{14}$) and antimony (Sb_1) [4].

The vacuum chamber was evacuated with an oil diffusion pump system; the ultimate pressure was 1.3×10^{-6} Pa and the sample was baked for 5–10 h. The substrate (Fig. 1) was fixed on tungsten heater and heated from 300 to 350°C. Decaborane was sublimated by heating at 85°C and was introduced into the vacuum chamber through a variable leak valve. Antimony metal (purity 6 N) was evaporated from the tungsten crucible by resistance heating. Furthermore we adopted cracking heater (W) converting Sb_2 into Sb_1 below the substrate (~ 5 cm) and operated at 1100°C. A molecular flux of the reactant gas was emitted simultaneously with the evaporated antimony molecules on the substrate under molecular flow region. The film was prepared at decaborane partial pressure of 7.2×10^{-2} Pa, and antimony partial pressure of 1.3×10^{-3} Pa and substrate temperature of 350°C. The film thickness of 0.5 μm was obtained. The composition of the film was $B_{12}Sb_2$ determined by XPS, which would be reasonable in analogy to $B_{12}P_2$ [5]. The crystallinity of the films was determined by X-ray diffraction to detect amorphous structure. The B–Sb bond was identified from IR spectra, overlapping with characteristic B–B bond.

As a reference material we prepared boron films on the substrate (Fig. 1) by the present method [6].

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Ohmic metal contacts were founded by evaporating Al at 200°C. The electrical properties of the $B_{12}Sb_2$ films were measured by van der Pauw method. A block diagram of thermoelectric measurement is found in Refs. [6,7]. The electrical conductivity of the films was measured by a two-probe method at temperatures between room temperature and 600°C under argon atmosphere. Thermoelectric voltage between hot and cold junctions was measured under a constant temperatures gradient of 2–3°C.

Thermal diffusivity of the present substrate was measured by laser flash method using a ring flash light method [8,9].

3. Result and discussion

3.1. Electrical properties at room temperature

Prior to measuring the electrical properties of the films, we tried to measure them for the present substrate (Fig. 1), but failed to measure because Si film was too thin.

The electrical properties of the film grown are shown in Table 1, together with a-B film on sapphire crystal by gas source molecular beam deposition [10] and Si-doped $B_{12}P_2$ [5]. The large differences in the hole concentrations are observed for the boron films. Higher carrier concentration for the present a-B film than GMBD ones [9] would be influenced by the silicon on the substrate (Fig. 1).

When we compare the present B film with $B_{12}Sb_2$ films, high hole mobility is observed for $B_{12}Sb_2$. This would be the characteristic $B_{12}Sb_2$. If we could prepare stoichiometric BSb film by controlling composition Sb/B, the mobility would increase. $B_{12}Sb_2$ films are p-type conductors, which would be reasonable by the analogy with the $B_{12}P_2$ [5]. Boron aggregation into B_{12} cluster would form intrinsic acceptor level in the band gap due to electron deficiency [11] showing p-type conduction. The present $B_{12}Sb_2$ film has higher carrier concentration, mobility and resistivity than Si-doped $B_{12}P_2$ [5], which would be due to a small energy band gap for boron antimonide. BP and $B_{12}P_2$ have band gaps 2.1 and 3.3 eV, respectively. Theoretical calculation of the band gap in BSb is 0.53 eV [2], and that of $B_{12}Sb_2$ is estimated to be 0.8 eV considering those in BP and $B_{12}P_2$.

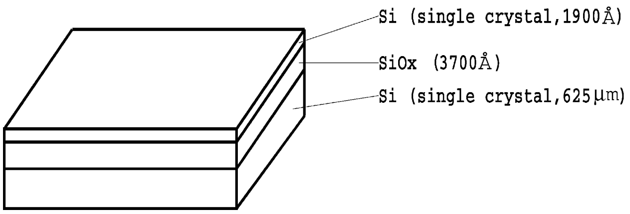

Fig. 1. The substrate (Si on SiO_x) in the experiment.

3.2. Thermoelectric properties

Thermoelectric properties of $B_{12}Sb_2$ films are influenced by such deposition condition as baking time in the chamber. Temperature dependencies of the electrical conductivity (σ) of the films are shown in Fig. 2, together with those of the boron films on sapphire crystal [6] prepared by the same method of the present experiment. The data for $B_{12}Sb_2$ films were prepared after baking for 10 h in the chamber. Temperature dependency of the electrical conductivity for the boron film by Nakamura [6] shows linear with respect to reciprocal temperature. On the contrary, the present boron film has high conductivity and almost constant

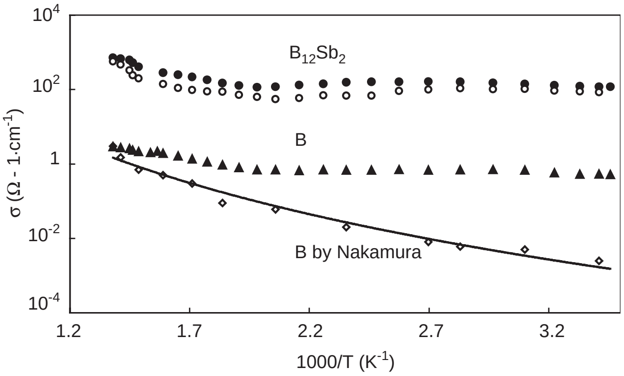

Fig. 2. Temperature dependence of electrical conductivity for $B_{12}Sb_2$ and B films. Result of amorphous MFPVD boron film by Nakamura [6] is also shown.

Table 1
Electrical properties of p-type boron and $B_{12}Sb_2$ films in comparison with those by gas source molecular beam deposition (GMBD) boron and Si-doped $B_{12}P_2$ wafer, respectively

Specimen	a-B film	a-B film by GMBD (10)	a-$B_{12}Sb_2$ film	Si-doped $B_{12}P_2$ wafer (5)
Resistivity (Ω cm)	0.91	1.7×10^4	0.19	6.2×10^4
Hall coeff. (cm^3/C)	16.9	3.9×10^5	18.7	6.7×10^4
Carrier concentration (cm^{-3})	3.7×10^{17}	1.6×10^{13}	3.3×10^{17}	9.3×10^{13}
Mobility (cm^2/V s)	15.5	18.1	98.9	10.8

conductivity up to 500 K, which would be expected to be the influence of the silicon on the substrate (Fig. 1). The conductivity of the $B_{12}Sb_2$ film becomes almost constant below 440 K, which would be caused by the silicon on the substrate. However, above 500 K conduction would become intrinsic with the expected band gap of 0.86 eV.

Temperature dependencies of thermoelectric power of the films are shown in Fig. 3. They are all p-type conductors, which are consistent with Hall effect measurement. Thermoelectric power for $B_{12}Sb_2$ films shows gradual decreases with increasing temperature and tends to saturate at 400 K. High α values of ~ 1 mV/K at around room temperature should be noted.

Fig. 4 shows thermal diffusivity of conventional Si wafer and the present substrate (Fig. 1) to calculate thermal conductivity of the substrate (κ). The present substrate (Fig. 1) has an effect to separate insulating SiO_x. Thermoelectric figure-of-merit (Z) based on the present substrate is shown in Fig. 5. Higher thermoelectric figure-of-merit of $\sim 10^{-4}$/K was obtained indicating that $B_{12}Sb_2$ films are promising for thermoelectronic materials.

Thermoelectric figure-of-merit (Z) is given by (1)

$$Z = \alpha^2\sigma/\kappa \infty m^{*3/2}(\mu/\kappa_{\mathrm{ph}}), \qquad (1)$$

where m^* is effective mass and κ_{ph} is phonon-thermal conductivity. Low electrical conductivity in Si-doped $B_{12}P_2$ produces lower thermoelectronic figure-of-merit, despite high thermoelectronic power [5]. However, the present $B_{12}Sb_2$ film with high electrical conductivity produces higher thermoelectric figure-of-merit than Si-doped $B_{12}P_2$ [5]. On the other hand the present $B_{12}Sb_2$ would be expected to have low m^* and with respect of the ratio of μ/κ_{ph}, it has been known that a mobility generally increased with increasing molecular weight of materials, in which the lattice thermal conductivity decreases. These facts would result in high Z for $B_{12}Sb_2$ films.

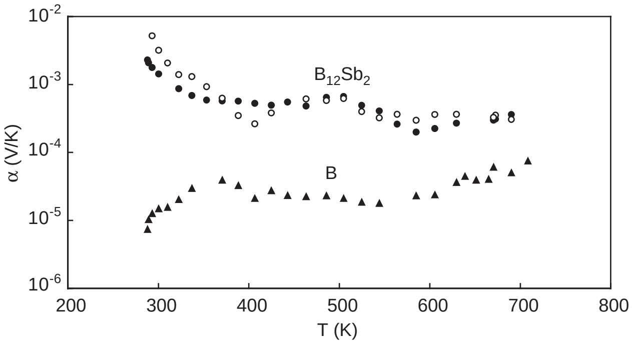

Fig. 3. Temperature dependence of thermoelectric power for $B_{12}Sb_2$ with reference to the boron film in the present experiment.

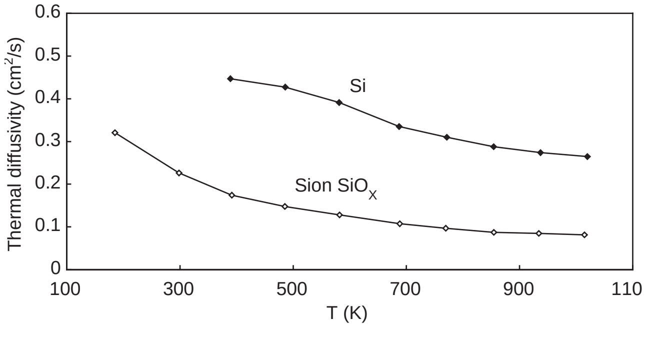

Fig. 4. Temperature dependence of thermal diffusivity of the substrate.

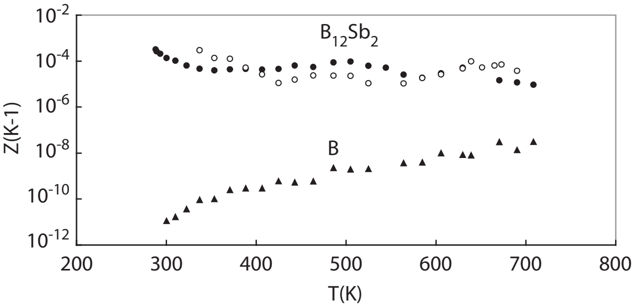

Fig. 5. Temperature dependence of thermoelectric figure of merit for $B_{12}Sb_2$. Result of the boron film is also shown.

4. Conclusion

Amorphous $B_{12}Sb_2$ films prepared for the first time by MFPVD process on Si (single crystal, 1900 Å)/SiO_x (3700 Å)/Si (100) (625 μm) display high mobility of ~ 100 cm^2/V s and high thermoelectric figures of merit of $\sim 10^{-4}$/K values, which makes the film promising candidates for new functional device materials.

Acknowledgments

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