THERMAL PROPERTIES OF BORON PHOSPHIDE SINGLE CRYSTALLINE WAFERS

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The present paper describes thermal properties of well-characterized boron phosphide single crystalline wafers prepared using chemical vapor deposition up to high temperatures. The thermal diffusivity was measured by using a unique ring flash light method. These crystals have large values of 1.8 cm^2/sec at room temperature and show a pronounced decrease at raised temperatures due to phonon scattering. Analysis of the specific heat capacity by the differential scanning calorimetry method induces the Debye temperature and the Grüneisen parameter, which demonstrate low atomic mass, strong interatomic bonding, high anharmonicity and low ionicity in boron phosphide. The thermal conductivity calculated by the products of thermal diffusivity, specific heat capacity and density of the wafer produces high thermal conductivity of 4.0 W/cm·K at room temperature and is comparable to that of boron nitride. Boron phosphide is a promising material for the heat sink substrates for semiconductor devices. The temperature dependence of the thermal conductivity almost coincides with the calculated lattice thermal conductivity by 3-phonon processes.

1. Introduction

The III-V compound semiconductors are attractive for thermal conductivity studies. These materials offer a wide range of lattice and electronic properties, and can be obtained in highly pure form, so that impurity effects are minimized and the intrinsic properties can be investigated and compared.

Thermal conductivity is also of technological importance. The thermal conductivity value is necessary for calculating the figure of merit for thermoelectric devices. For power dissipating devices such as diodes, transistors or lasers it is useful to know the value of the thermal conductivity to assist in device and circuit design.

Boron phosphide (BP), a III-V compound semiconductor with a wideband gap, is a promising material for application in thermoelectric devices operating at high temperatures[1)-3)]. Thus, the thermal conductivity of BP is important for determining the thermoelectric figure of merit. However, there have been two reports, one on single crystalline wafers above room temperature[1)] and one on small single crystals below room temperature[4)]. Moreover, the thermal conductivities at room temperature differ by two orders of magnitude[5)]. Therefore, the main object of the present paper lies in the measurement of thermal diffusivity by the modified laser flash method, because the conventional laser flash method has many problems when applied to thick wafers. The present paper describes thermal characteristics of well-characterized boron phosphide single crystalline wafers made by the CVD process[6)] in order to clarify their intrinsic thermophysical properties.

2. Theoretical

The specific heat gives the value of Debye temperature θ, and Grüneisen parameter γ. θ is obtained from the specific heat at constant volume C_V, which is deduced by the usual thermodynamic formula:

$$C_V = C_P - (\beta^2 V/K)T \tag{1}$$

where $\beta=3\alpha$ is the coefficient of volume expan-

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sion, K the isothermal compressibility, and V the molar volume. With the values[7] of $K=5.3\times10^{-13}$ cm^2dyn^{-1}, $V=14.07$ cm^2mol^{-1} and the published data on α[8], C_P is converted to C_V. θ is calculated by the following formula:

$$C_V/6R = (3/x^3)\int_0^x[x^4e^x/(e^x-1)^2]dx \tag{2}$$

$$x = \theta/T \tag{3}$$

where R is the gas constant of 1.987 $cal\cdot mol^{-1}\cdot K^{-1}$. The values of the right-hand terms in Eq. (2) are tabulated[9].

γ is calculated by the following formula:

$$\gamma = \beta V/KC_V = 3\alpha V/KC_V. \tag{4}$$

We have solved the difficulty in the laser flash method of measuring the thermal diffusivity of a wafer by using a ring flash light, which originates from multi-variable analysis in a two-dimensional model. Details of this method will be described elsewhere[10]; we will mention only the outline. Here we consider the cylindrical coordinates for a homogeneous cylinder as shown in Fig. 1. r_0 indicates the region where the temperature is measured. When laser light irradiates the specimen in the form of a ring with an inner radius r_1 and an outer radius r_2, the temperature from the central axis to the radius r of the disk $T(x,r,t)$ can be derived from general solutions of the heat conduction equations for cylindrical samples[11], given by

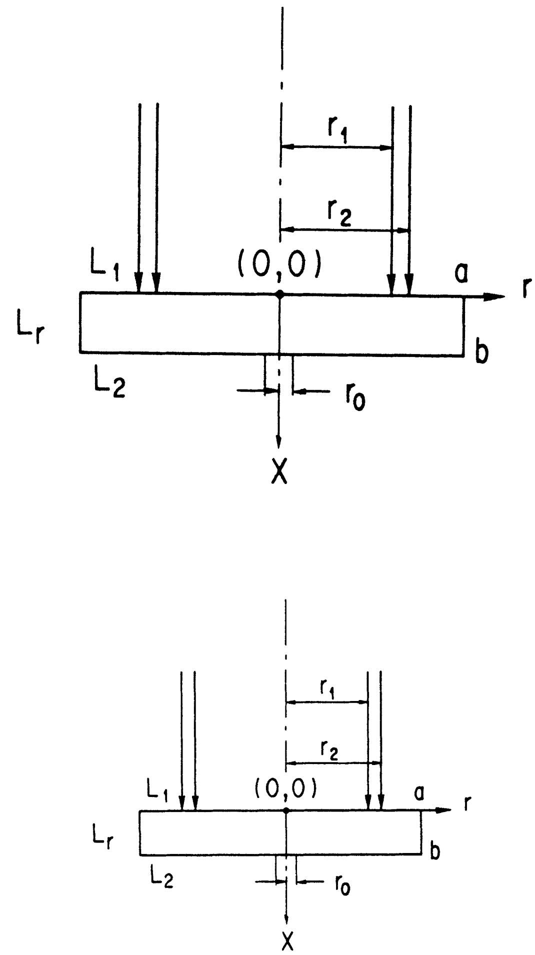


Fig. 1. Coordinates for the sample by ring flash laser.

$$T(x,r_0,t) = T_0\Sigma Y_i(x)Y_i(0)\Sigma H_j(r_0)G_j\exp(-C_{ij}t) \tag{5}$$

$$Y_1(x) = 2^{1/2}(\beta_i^2+L_2^2)^{1/2}(\beta_i\cos\beta_i(x/b) + L_1\sin\beta_i(x/b)/b^{1/2}\{(\beta_i^2+L_i^2)\cdot(\beta_i^2+L_2^2+L_2)+L_1(\beta_i^2+L_2^2)\}^{1/2} \tag{6}$$

$$G^j = (2a/Z_j)(r_2J_1(Z_jr_2/a) - r_1J_1(Z_jr_1/a))/(r_2^2-r_1^2) \tag{7}$$

$$H_j(r_0) = \frac{(2aZ_j/r_0)J_1(Z_jr_0/a)}{(Z_j^2+L_r^2)J_0^2(Z_j)} \tag{8}$$

$$C_{ij} = -\alpha(Z_j^2/a^2+\beta_i^2/b^2) \tag{9}$$

$$\tan(\beta_i) = \beta_i(L_1+L_2)/(\beta_i^2-L_1L_2) \tag{10}$$

$$Z_jJ_1(Z_j) - L_rJ_0(Z_j) = 0 \tag{11}$$

where $T_0=Q/Cp\pi a^2b$ and $\kappa=\alpha\rho C$. J_0 and J_1 are the 0th and 1st order Bessel functions, respectively. β_i and Z_j are positive roots of Eqs. (6) and (7), respectively; α, κ, ρ, C, Q, and Lm represent the thermal diffusivity, thermal conductivity, density, heat capacity, absorbed energy of the disk and the dimensionless number of heat loss ($m=1$: irradiating face, $m=2$: rear face and r: the side), respectively.

3. Experimental

The BP wafers[6] were grown on (100)- and (111)-oriented Si substrates by the thermal decomposition of diborane (1% in hydrogen) and phosphine (5% in hydrogen) in a hydrogen atmosphere (3 l/min) at 950°C and 1050°C for Si(100) and 1000°C for Si(111). The growth was made at gas-flow rates of 20, 300 or 500, and 3000 cm^3/min for diborane, phosphine, and hydrogen respectively in these temperatures at deposition times of 24–28 hrs. BP wafers with areas of 10×20 mm^2, and thicknesses of 200–300 μm, were obtained by dissolving away the Si substrate in an $HF–HNO_3$ solution.

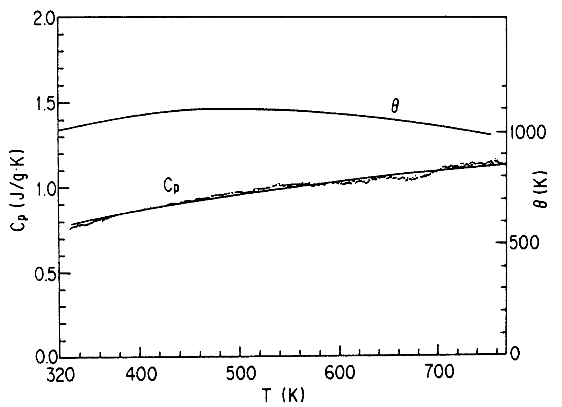
The specific heat capacity was measured on small wafers (4×4 mm^2) of boron phosphide by differential scanning calorimetry (Perkin-Elmer, DSC-2) in the temperature range of 60~500°C with the use of automatic data processing and calibration procedures.

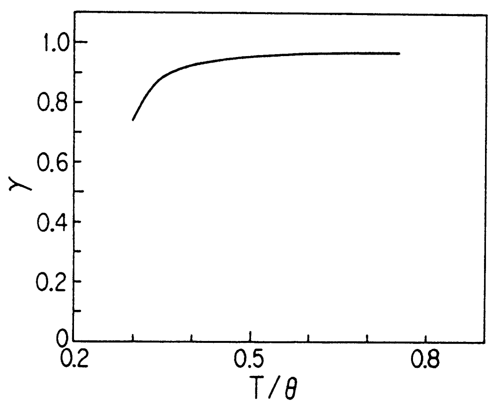
The process of calculating the thermal diffusivity is as follows; First, the known parameters a, b, r, i and j are specified by measuring conditions. Second, initial values of unknown parameters such as α, T_0 and Lm are presented. Finally, after the identifying values of β_i and Z_j, the unknown parameters were estimated by curve fitting.

The measurements were performed on graphite and sapphire with a thickness of 0.5 mm and an area of 10×10 mm^2 to confirm that they coincide with standard literature values. Graphite-coated thin films with a thickness of ~5 μm were sprayed on both faces of the specimen by dry graphite film lubricant (dgf 123).

4. Results and discussions

Figure 2 shows the specific heat capacity of BP(100). The specific heat capacity increases with





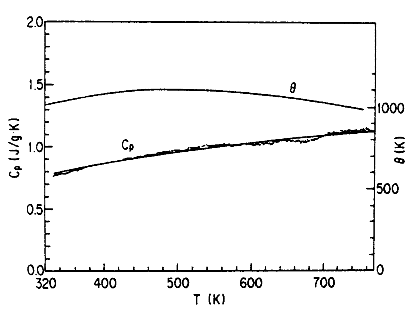


Fig. 2. Temperature dependencies of specific heat capacity (C_P) and Debye temperature (θ) of n-BP(100) wafers.

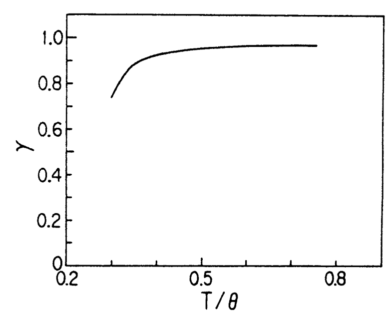


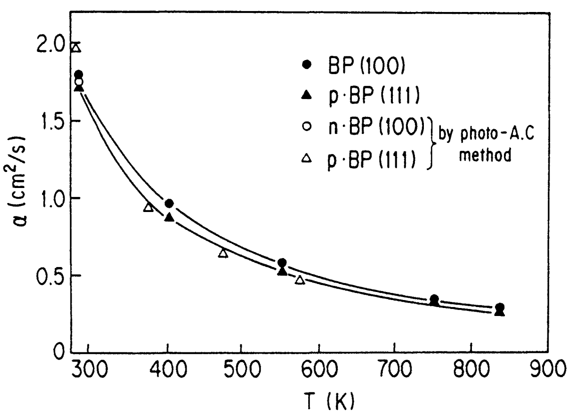
Fig. 3. Grüneisen parameter of BP as a function of reduced temperature.

increasing temperature, but no appreciable difference between the (100) and (111) planes or the p-and n-types was observed.

The temperature dependence of θ is also shown in Fig. 2. Ohsawa *et al.*[7] obtained a Debye temperature of 960±50K at 300K by measuring the specific heat capacity using AC calorimetry. The difference in Debye temperatures between theirs and ours would be caused by the measurement method used. The Debye temperature and its temperature dependence of the presented crystal should exhibit the features of boron phosphide; a high Debye temperature reflects the low atomic mass and strong interatomic bonding in boron phosphide. Figure 3 shows γ as a function of reduced temperature T/θ. Small γ means high anharmonicity, and the small variation would be attributed to its low ionicity.

The temperature dependencies of thermal diffusivity together with that obtained by the photo-AC method are shown in Fig. 4. A fairly good agreement between the two methods is established, which justifies the present ring flash light method. The thermal diffusivity has a large value of 1.8 $cm^2 \cdot s^{-1}$ at room temperature and shows a pronounced decrease with increasing temperature due to phonon scattering.

The temperature dependence of thermal conductivity as calculated from the product of the thermal diffusivity, specific heat capacity and density is shown in Fig. 5. The thermal conductivity of BP single crystalline wafers is ~4.0 $W \cdot cm^{-1}K^{-1}$ at room temperature, which is in good agreement with Slack's data[4] and is comparable to that of boron nitride. The high thermal conductivity of boron phosphide is similar to that of other adamantine compounds[4]. Boron phosphide is thus



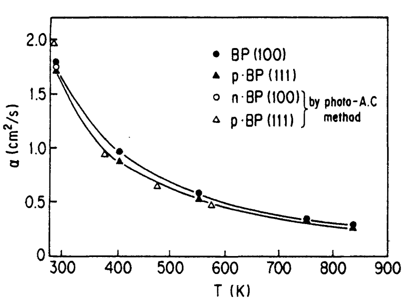
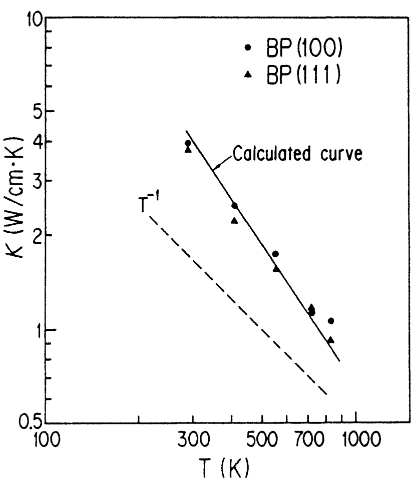


Fig. 4. Temperature dependence of thermal diffusivity of various BP wafers.



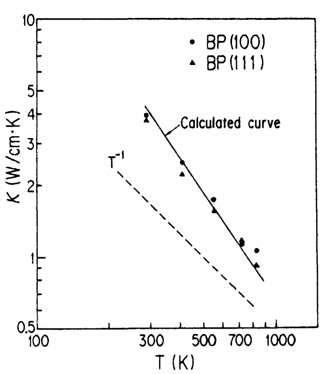


Fig. 5. Temperature dependence of thermal conductivity of BP wafers.

a promising material for heat-sink substrates for semiconductor devices. In the present single crystalline wafer, the phonon scattering predominates so that the thermal conductivity decreases with increasing temperature with a slope of $\log\kappa$ vs $\log T$ plot close to -1. As BP is a semiconductor, the electronic contribution to thermal conductivity is small. Thus, the thermal conductivity in Fig. 5 would correspond to lattice thermal conductivity.

The lattice thermal conductivity for 3-phonon processes at high temperatures is given by[12)]

$$\kappa_1 = (3/5)4^{1/3}(k/h)^3 M\delta\theta^3/\gamma^2 T \qquad (12)$$

where M is the mean atomic mass, δ is the cubic root of the atomic volume. κ_1 is calculated by the values of θ (Fig. 2) and γ (Fig. 3). The result is shown in Fig. 5 as a solid line in very good agreement with the experimental result, so that thermal conduction should be performed by 3-phonon processes.

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