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Electrical Properties of Well-Characterized BP Wafers up to High-Temperatures

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Electrical properties of well-characterized BP wafers have been investigated in the temperature range between room temperature and 850°C. It is confirmed that the autodoping of Si from the substrate occupies the phosphor site in BP acting as an acceptor. Some electronic transport properties such as donor and acceptor levels, and the lattice scattering process are clarified. Mobility of 30cm^2/s.V at 850°C for n-type would indicate that BP is a promising material for devices operated at high temperatures.

1. INTRODUCTION

Boron phosphide (BP), one of the III-V compound semiconductors, is known as a refractory semiconductor with a wide band gap and has potential ability of the application for electronic devices in extreme condition[1].

Recently, some works have been reported concerning device characteristics of BP such as Si-BP-Si double heterojunction[2], p-n junction[3], Schottky diodes[1,4] and thermoelectric device[5].

In order to develop the electric devices operated at high temperatures, the electrical properties at high temperature should be clarified. As for electrical properties, there are some data[6-8] on conductivity or conductance of BP as a function of temperature up to 1000K to calculate the energy levels of donor or acceptor. Hence, the present report is the first one concerning the systematic studies on the electrical properties, i.e., conductivity, carrier concentration and mobility of BP at high temperature up to 850°C. As a result, the basic conduction behavior of BP and its utility for device available at high temperatures are clarified. The present paper describes the characterization of BP wafers by various epitaxial conditions and the electrical properties at high temperature in relation to the conduction mechanism.

2. EXPERIMENTAL

The BP wafers were grown on the (100)- and (111)-oriented Si substrates by the thermal decomposition[9-11] of diborane (1% in hydrogen) and phosphine (5% in hydrogen) in a hydrogen atmosphere at 950°C (No.1) and 1050°C (No.3 and 4) for Si(100), and 1000°C (No.2) for Si(111). The growth was made at gas-flow rates of 20, 300 (No.4) or 500 (No.1-3) and 3000cc/min, for diborane, phosphine and hydrogen, respectively, at those temperatures in the deposition time of 24-28hrs. BP wafers with the area of 10x20mm^2, thickness of 200-300μm, were obtained[11] by solving away the Si substrate in an HF-HNO_3 solution. The wafers were almost transparent. All wafers were confirmed to be single crystals[11].

To make identification of the impurity species, a secondary-ion-mass spectrometric (SIMS) analysis was made. The ion probe analyser was a commercial one of scanning type (A-DIDA 3000, Seiko Industry and Electronics LTD). A primary oxgen-ion beam struck the sample at the normal incidence in the vacuum of 10^{-9}Torr.

The lattice constant was measured precisely by Bond method. The electrical properties of wafers were studied by van der Pauw method at temperatures between room temperature[1,4,11] and 850°C[12].

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION

The electrical resistivity ρ, carrier concentration n and mobility μ measured by van der Pauw method are shown in Table 1. The results of precise measurements of the lattice constants are shown in Table 2, being calibrated by thermal expansion coefficient[13]. The conduction types of BP are determined by excess boron or phosphor as

Table 1 Semiconducting properties of BP wafers

Orientation	Type	ρ (Ω.cm)	n(cm^{-3})	μ(cm^2/s.V)
No.1 (100)	n	0.15	3.7×10^{17}	120
No.2 (111)	p	12.5	1.6×10^{16}	36.5
No.3 (100)	n	2.5	2.5×10^{16}	107
No.4 (100)	p	10.0	3.1×10^{16}	20.0

Table 2 The precise lattice constant of BP wafers

Orientation	Type	Reflection	Half band width	Lattice constant (Å)
No.1 (100)	n	(400)	0.13°	$4.538675\pm3\times10^{-6}$
No.2 (111)	p	(333)	0.14°	$4.537983\pm3\times10^{-6}$
No.3 (100)	n	(400)	0.15°	$4.538467\pm7\times10^{-6}$
No.4 (100)	p	(400)	0.14°	$4.538205\pm6\times10^{-5}$

p or n, respectively[14,15].

The result of analysis by SIMS indicates that the majority of impurities was Si. In addition to Na, K, Ca and Cr, special impurities such as Mn, Co and Mg were detected for No.3, Mg, Ti, V, Mn and Co for No.2 and Mn, Co and Ni for No.4.

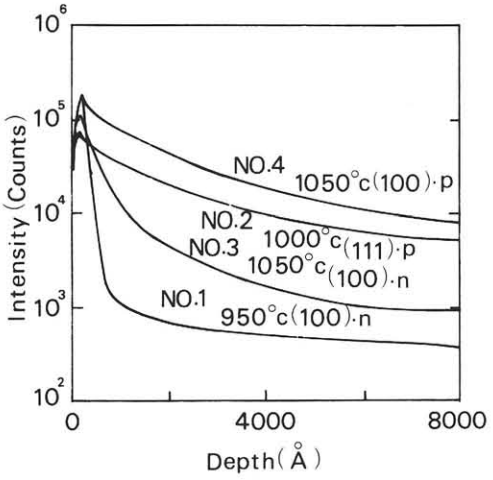

Fig.1 Si profiles at the substrate sides for four BP wafers used in the experiment.

The Si profiles at the substrate side (Fig.1) indicate the autodoping of Si from the substrate and its dependence on the growth temperature and plane[16]. Ohsawa et al. [16] examined the Si contamination of the epitaxial n-type BP layer grown on the Si substrate by BCl_3-PCl_3 system. They showed the contamination by Si as much as 1% and correlated it with carrier concentration in the range of 10^{17} to 10^{20} cm^{-3}, i.e., the carrier concentration increased with increasing Si contents. They concluded that Si atoms would act as donor and would be incorporated at boron sites in BP. In the present case, the contents of Si in BP would be expected to be far smaller than theirs. The carrier concentration decreases with increasing Si content for the n-type specimen (No.1 and 3, and Fig.1) and vice versa for the p-type one (No.2 and 4, and Fig.1), which indicate that Si atoms act as acceptor and are incorporated at phosphor site in BP.

Next, we would like to mention about the lattice constant in relation to the conduction type. The excess phosphors occupy the boron sites in BP lattice, and vice versa for p-type[4]. The ionic radii of boron, phosphor and silicon in BP are expected to be 0.88, 1.10 and 1.17 Å, respectively. Then the lattice shrinks in p-type (No.4), whereas it expands in n-type (No.3). The wafer No.1 with more excess phosphors than No.3 expands the lattice broader than No.3 while the wafer No. 2 with more excess borons than No.4 shrinks the lattice narrower than No.4.

The difference in the ionic radii of phosphor and silicon is not so large that no appreciable effect of Si on lattice constant should be expected.

3.2 HIGH TEMPERATURE CHARACTERISTICS

Temperature dependencies of the conductivity σ, carrier concentration n or p, and Hall mobility μ are shown in Fig.2 and 3 for n and p-types, respectively. The temperature dependency of conductivity for n-type sample (Fig.2) is understood as the competition of the decrease of mobility and the increase of carrier concentration.

The plots of log n vs 1/T show linear relation at the temperatures between room temperature and 850°C. From the slopes, we obtained the activation energy of donor E_d, assuming $n\sim\exp(-E_d/2kT)$, where k is Boltzman constant. The donor energies of 0.1eV for No.1 and 0.25eV for No.3 seem to

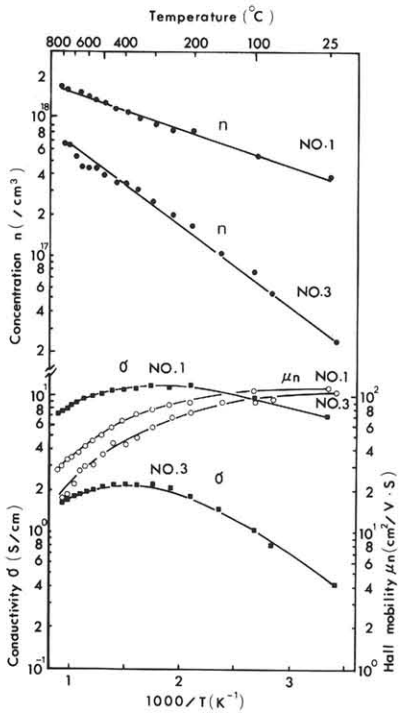

Fig.2 Temperature dependencies of conductivity σ, carrier concentration n and Hall mobility μ_n of n-BP(100).

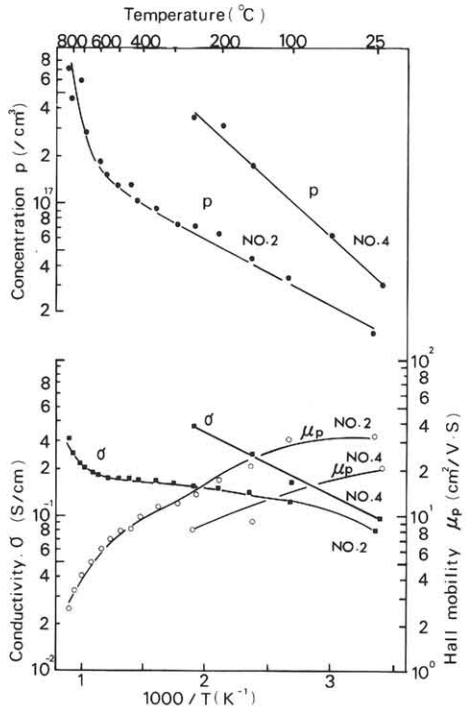

Fig.3 Temperature dependencies of conductivity σ, carrier concentration p and Hall mobility μ_p of p-BP.

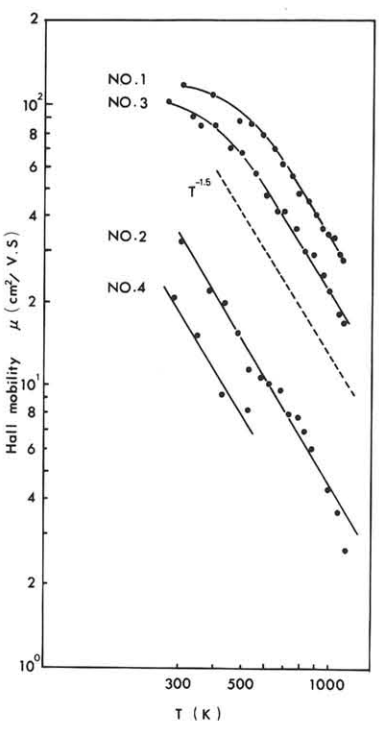

Fig.4 Hall mobility of four BP wafers as a function of temperature.

correspond to the double donors of phosphor (P^{++}) and impurities donors such as Mg, Mn and Co, respectively. The conduction in the sample No.1 is performed by the excitation of double donors. No.3 contains much impurities than No.1, then double donors drop down to the impurity levels and excitations take place from these levels. This is consistent with the data that the mobility for No.3 with some impurities is lower than that for No.1. The slopes of the conductivity and electron concentration show nearly the same value, so the donor levels reported, lying about 0.1eV[7,8] and 0.18eV[8] below the conduction minimum, would correspond to the double phosphors and impurities levels, respectively.

The behaviors for p-types (Fig.3) are different from those for n-types. The mobility for p-type is lower than that for n-type. Then, we could not obtain the data for No.4 above 200°C because of the fluctuation of lower Hall voltage. The activation energy in the sample No.2 is calculated to be 1.8 eV above 650°C, which is nearly equivalent to the band gap of 2.0eV and corresponds to the intrinstic conduction region. This is due to the fact that the carrier concentration for No.2 is lower than other n-type samples (Fig.2).

The intrinsis ionization with activation energy of 1.95eV at a temperature above 1000K was also reported by Chu et al.[6] who measured the electrical conductance of p-type BP grown on the SiC (0001) plane by BBr_3-PCl_3 system.

The activation energy of acceptor is 0.20 and 0.32eV for No.2 and No.4, respectively. We could not obtain the p-type wafer with lower Si content as No.1. The p-type wafers contain more Si than n-type's (Fig.1) and also contain some impurities, so that the conduction by double acceptors of B^{--} would be replaced by Si and/or impurity acceptors.

The Hall mobility of four wafers are shown in Fig.4 as a function of temperature. The mobilities for n-types range from 120-106 to 80-50 $cm^2/s.V$ between room temperature and 600K. Above 600K, log μ's are linear to log T for n-types. The mobilities decrease to 20-30$cm^2/s.V$ at 800°C. Mobility of 30$cm^2/s.V$ at 850°C would indicate that BP is a promising material for devices

available at high temperatures. The mobility for p-type show linear dependence in the log μ vs log T plots in the entire temperature range. The value α in the relation $\mu \sim T^{\alpha}$ determimed from the slope of log μ vs log T plots is -1.5, so that the lattice-phonon scattering prevails in the scattering process at these temperature ranges. At high impurity concentrations or at low temperatures, the lattice scattering does not predominate, but the mobility is limited by scattering by impurity centers, which corresponds to the case with No.1 and 3 at the temperature up to 600K. At high temperature, the lattice scattering predominates. The increasing thermal agitation of lattice leads to a shorter distance where the carriers travel between collisions with the lattice, and the carriers travel faster at high temperatures, thus shortening the time between collisions, these factors serve to decrease the mobility as $T^{-1.5}$.

4. CONCLUSION

We have prepared BP wafers with p- and n-types by controlling the flow rate of phosphine or substrate temperature in the chemical vapor deposition using B_2H_6-PH_3 system. The autodoping of Si from the substrate determined by SIMS occupies phosphor site in BP acting as an acceptor, and also explains the data on the electrical properties and lattice constants. We have measured electrical properties of well-characterized BP wafers up to high temperature of 850°C so that donor and acceptor levels such as double donors of phosphine, impurity donors and Si and/or impurity acceptors, and the lattice scattering process have been clarified. Mobility of 30cm^2/s.V at 850°C for n-type is considered to be promising for devices available at high temperatures.

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