Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 419-422

Schottky Barrier Diodes Using Thick Wafers of Boron Phosphide

Yukinobu Kumashiro, Yasumasa Okada and Shun-ichi Gonda

Electrotechnical Laboratory

1-1-4 Umezono, Sakura-Mura, Niihari-Gun, Ibaraki, Japan

Thick single crystalline wafers (200~300 μm) of BP were grown by chemical vapor deposition technique. The wafers were characterized by the measurements of X-ray transmission Laue pattern. RHEED pattern, lattice constants by Bond method and electrical properties by Van der Pauw method. Two types of Schottky barrier diodes, i.e., n.BP-Sb and p.BP-Au, were fabricated. The n.BP-Sb diode has an excellent characteristics, that is, a reverse voltage of 5 V and a built-in potential of 1.5 V while those of the p.BP-Au diode are 1 V and 1.0 V.

1. Introduction

Boron phosphide (BP), one of III-V compound semiconductors with wide gaps, has high melting point, high hardness, excellent stability, and high oxidation resistance at high temperatures and it can be n- and p-type materials. This material has potential application for electronic devices in extreme condition.

However, BP has been considered to have few outstanding features from the view point of device application. Few works were reported concerning device fabrication. This is caused by the difficulty in preparing well-characterized single crystals, because the melting point is above 3000°C and decomposition begins from about 1130°C under 1 atm.

Among various crystal growth techniques, epitaxial growth by chemical vapor deposition (CVD) process is one of the most eminent methods for obtaining high purity thick wafers for device purpose. Nishinaga et al[1] found for the first time that BP would grow epitaxially on (100)- and (111)- oriented Si substrates by thermal reduction of a BBr_3-PCl_3 mixture with hydrogen. Shohno et al[2] studied the growth of BP on (100)-, (110)- and (111)- orientated Si substrates by thermal decomposition of a B_2H_6-pH_3 mixture in hydrogen atmosphere. They also fabricated several combination of BP-Si heterostructures for the purpose of a wide gap window solar cell of nBP nSi-pSi structure[3] and a wide gap emitter transistor with nBP nSi-pSi-nSi structure[3]. Multilayer epitaxial growth of BP and Si has been proposed with the aim of three-dimensional intergration in Si layers isolated with a wide gap semiconductor[4-6].

BP is another canditate materials for thermoelectric device[7] due to high thermoelectric powder (500μV/K at 1000K).

We are proposing a solid state neutron detector utilizing large neutron capture cross section of Boron and making an effort to fabricate BP diodes. As for BP Schottky diodes, there has been only one work on n.BP-Sb type[8], but no paper on p.BP wafers. There was a datum on the barrier height of p.BP-Au determined by photoresponse measurement[9].

The present paper describes the growth of BP thick single crystal wafers by CVD process and the fabrication of two types of Schottky barrier diodes, i.e., n.BP-Sb diode with excellent characteristics and p.BP-Au diode.

2. Experimental

The BP wafers were grown on (100)- and (111)-oriented Si substrates by chemical vapor deposition. Diborane (B_2H_6) and phosphine(PH_3), diluted to 1% and 5% in hydrogen, respectively, were used as reactant gases. The CVD apparatus used was nearly the same as Shohno et al's[2]. A reaction chamber made of fused quartz was placed in a position slighly inclined and a SiC coated graphite susceptor was placed in the chamber in a horizontal position. The susceptor was heated externally by an RF generator. After heat treatments of susceptor and substrate[2], the two reactant gases were mixed with hydrogen at the growth temperature.

Growth was made at gas flow rates of 20, 250-500 cc/min and 3 l/min, for diborane, phosphine and hydrogen, respectively, in the temperature range of 950 to 1050°C at deposition times of 24-28 hrs. BP wafers were obtained after removing off the Si substrate in a solution of HF-HNO_3. Crystal quality was evaluated from surface morphology, X-ray Laue photograph and RHEED pattern. Lattice constants were precisely measured by Bond method. Electrical resistivity, carrier concentration and mobility were measured by Van der Pauw method.

Schottky barrier diodes were fabricated as follows. After the surface treatments by molten NaOH and by HF solution, ohmic contacts of the back face of the wafers were made by evaporation of Al, followed by annealing in argon at 410°C for 1 hr. The surface of the wafers were treated again with HF for a moment. Schottky barrier diodes were made using mask by evaporation of Sb and Au on n and p type BP, respectively. During evaporation, BP wafers were heated up to about 300°C. The diameter of the metal Schottky contact is 0.1mm. Current-Voltage characteristic of diode was observed by a curve tracer and the barrier capacitance was measured with a C-V profiler.

3. Results and Discussion

BP wafers with the square of 10 x 20 mm^2, thickness of 200-300 μm, were obtained. The wafers are almost transparent, but colored with orange-red and dark-red for the n- and p-types, respectively. The wafers are all single crystals confirmed by the surface morphology, X-ray transmission Laue photogragh and RHEED pattern[10]. An X-ray transmission Laue photogragh of the (100) wafer shows four-fold symmetry, indicating that BP grows epitaxially on the (100) Si substrate. On the other hand the (111) wafer inclines to the (100) plane with respect to the [100] direction, which is confirmed by a back reflection Laue photogragh and is pronounced in the RHEED pattern[10].

Electric reristivity ρ, carrier concentration n and mobility μ measured by the Van der Pauw method are shown in Table 1. The conduction types of BP are determined by excess boron or phosphorous as p or n, respectively[11,12]. The present wafers have the lowest carrier concentration reported so far.

The results of precise measurements of lattice constants are shown in Table 2, being calibrated by thermal expansion coefficient[13]. X-ray powder patterns of three n-type BP wafers grown epitaxially on (100)-Si and (111)-Si substrates by Mizutani et al[13] indicate that the lattice constant is 4.538 and 4.542Å for BP on (100)-Si and (111)-Si, respectively. As for (100) wafers, their results are in good agreement with our's, but the discrepancy is large for (111) wafers. In the present case, different lattice constants for n- and p-types should be noted. As is mentioned above, the excess phosphors occupy the boron site in the BP lattice for n-type and vice versa for p-type.

Table 1 Semiconducting properties of BP wafers

Orientation	Type	ρ (Ω.cm)	n(cm^{-3})	μ(cm^2/s.V)
(100)	n	0.41	1.0×10^{17}	145
	p	7.7	1.4×10^{17}	5.7
(111)	p	5.64	3.1×10^{16}	36.5

Table 2 The precise lattice constant of BP wafers

Orientation	Type	reflection	half band width	Lattice constant
(100)	n	(400)	0.13°	$4.538675\pm3\times10^{-6}$Å
(111)	p	(333)	0.78°	$4.535710\pm2\times10^{-6}$Å

The ionic radius of boron and phosphorus in BP are expected to be 0.88 and 1.10Å, respectively. Therefore, the lattice shrinks in p-type, and expands in n-type, which is reflected in the lattice constant (Table 2). Thus, the results of precise measurements of lattice constant, probably, explain the conduction type of BP.

The current-voltage characteristics of n. BP-Sb and p.BP-Au diodes are shown in Fig.1 and 2, respectively. The n.BP-Sb Schottky diodes by heat treatment of BP wafers during evaporation show excellent I-V characteristics (Fig.1b). This holds to other III-V compound semiconductor such as GaAs, in which it was heated during metal evaporation to drive off wafer or other vapours adsorbed on the surface of the semiconductors. Backward voltage is about 5V, which is the highest value ever known. Takenaka et al[8] obtain the backward voltage of 0.6V though there is no large difference between theirs and ours with respect to fabrication process. The large difference between them lies in the carrier concentration of BP wafer. Their wafers have a carrier concentration of 8×10^{17} cm^{-3}, which is far larger than ours (Table 1). In case of p.BP-Au diodes, however, heating process during Au evaporation does not alter I-V characteristics and the backward voltage is 1V (Fig. 2).

The barrier capacitance for n.BP-Sb and p. BP-Au Schottky barrier diodes is shown in Figs.3 and 4, respectively. The plot of $1/C^2$ against bias voltage (Fig. 3) in the same diode as Fig. 1b, shows slight deviation from straight line.

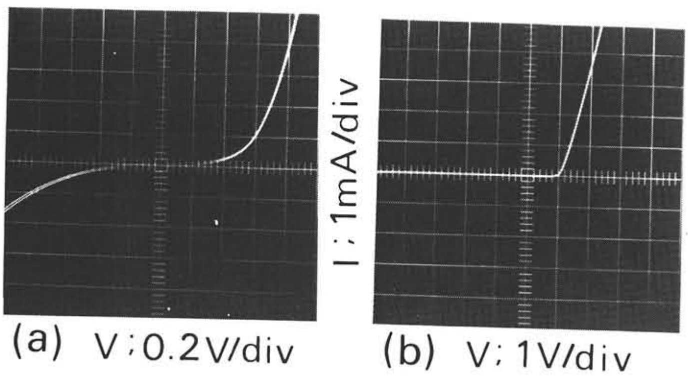

Fig.1 I-V characteristics of n.BP-Sb Schottky barrier diodes. (a) without heating of BP. (b) heating of BP during evaporation.

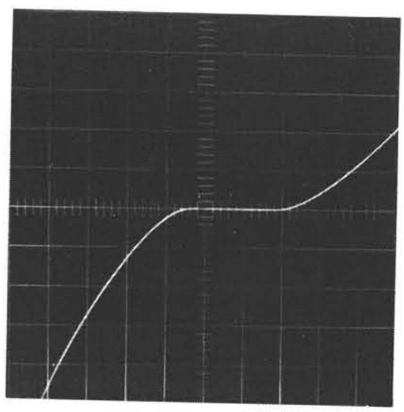

Fig.2 I-V characteristic of p.BP-Au Schottky barrier diode, V;0.5V/div, I;0.1mA/div.

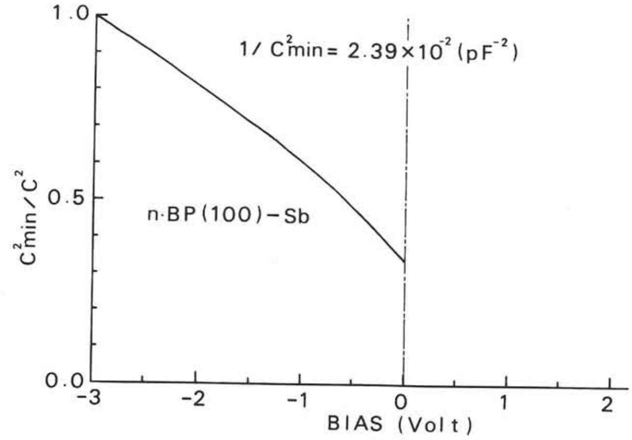

Fig.3 Reverse bias capacitance versus applied bias voltage for n.BP-Sb Schottky barrier diode. The barrier diode is the same as shown in Fig. 1 (b).

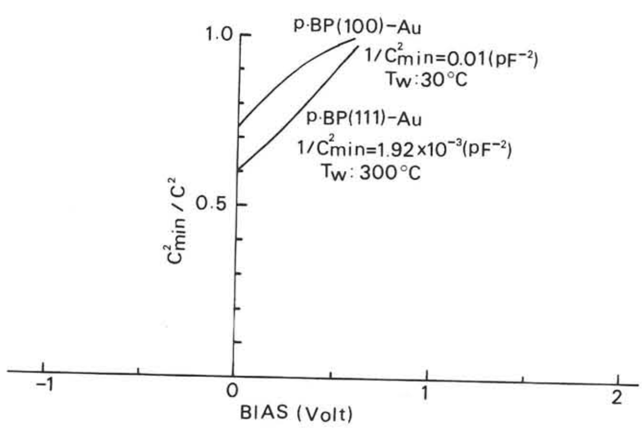

Fig.4 Reverse bias capacitance versus applied bias voltage for p.BP-Au Schottky barrier diode. Tw: wafer temparature during evaporation of Au. The barrier diode (Tw = 300°C) is the same as shown in Fig.2.

This is due to the non-uniformity of the donor density at the edge of depletion region, which is confirmed by the measurement of carrier density profiles. The width of depletion layer is 1000Å. Takenaka et al[8] obtained linear relation of $1/C^2$ with bias voltage and the built-in potential of 0.5V by extrapolation. When we extrapolate the $1/C^2$ vs V curve in Fig.3 from near zero volt region, the built-in potential is 1.5V which would be rather reasonable in considering the fact that the barrier height in n-type is (2/3) Eg, where Eg is the band gap. The linear relation of $1/C^2$ vs bias volt is observed for the p.BP(111)-Au diode fabricated without heating during evaporation of Au, but the extrapolation gives the built in potential of 2.57V, which is unreasonable value. Then, the heating of the wafer at about 300°C during evaporation brings the $1/C^2$ vs V (Fig.4) with the built-in potential of 1.0V, which is in fairly good agreement with p.BP (100)-Au and is reasonable value in considering the barrier height of 0.87eV by photoresponse method[9], though no difference is observed in I-V characteristiecs.

Like other semiconductors, the capacitance characteristics of p-type are inferrior to those of n-type. This would be due to the fact that Fermi-level pinning at the surface level in p-type semiconductor situates near the valence band and barrier height becomes lower than n-type. Then the fabrication of diodes with excellent characteristics is difficult in p-type.

4. Conclusion

Thick single crystalline wafers (200-300 μm) of BP were obtained by chemical vapor deposition using the B_2H_6-pH_3-H_2 system. Semiconducting properties of these crystals are excellent so that n.BP-Sb Schottky barrier diode with the highest reverse voltage shows almost linear relation of $1/C^2$ vs V with the built-in potential of 1.5V, although there remain some problems to improve the characteristics in p.BP-Au diode with the reverse voltage of 1V as built-in potential of 1.0V. From these result device application of BP is considered to be promising.

Acknowledgement

The authors wish to acknowledge K. Okamoto, K. Ishikawa and T. Miyazawa for valuable contribution. Appreciation is expressed to S. Yoshida and S. Misawa for the characterization by RHEED and electrical measurements and is also expressed to M. Yamanaka and Y. Hayashi for their valuable suggestions.

Reference

1) T. Nishinaga, H. Ogawa, H. Watanabe and T. Arizumi: J. Crystal Growth, 13/14 (1972) 346.
2) M. Takigawa, M. Hirayama and K. Shohno: Jap. J. Appl. Phys., 13 (1974) 411.
3) T. Takenaka, M. Takigawa and K. Shohno: J. Electrochem. Soc., 125 (1978) 634.
4) Y. Hirai and K. Shohno: J. Crystal Growth, 42 (1977) 124.
5) K. Nonaka, C. J. Kim and K. Shohno: J. Crystal Growth, 50 (1980) 549.
6) K. Shohno and C. J. Kim: J. Crystal Growth, 56 (1982) 511.
7) S. Yugo and T. Kimura: Phys. Stat. Sol., (a)59 (1980) 363.
8) T. Takenaka, M. Takigawa and K. Shohno: Jap. J. Appl. Phys., 15 (1976) 2021.
9) C. A. Mead: Solid-State Electronics, 9 (1966) 1023.
10) Y. Kumashiro, Y. Okada and S. Gonda: J. Crystal Growth (to be published).
11) K. shohno, M. Takigawa and T. Nakada: J. Crystal Growth, 24/25 (1974) 193.
12) S. Motojima, Y. Miura, K. Sugiyama and Y. Takahashi: Bull. Chem. Soc. Japan, 48 (1975) 3161.
13) T. Mizutani, J. Ogawa, T. Nishinaga and S. Uchiyama: Jap. J. Appl. Phys., 15 (1976) 1305.