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# Heteroepitaxial growth of boronphosphide III-V semiconductor on silicon by organometallic chemical vapor deposition

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**Crystallographic features of boronmonophosphide (BP) semiconducting layers grown directly on (111)Si by a triethylboran/phosphine atmospheric-pressure MOCVD system were investigated by X-ray diffraction and transmission electron diffraction (TED) techniques. The unintentionally-doped BP layers grown at 1025°C with an input $PH_3/(C_2H_5)_3B$ ratio of about 150 had transparent mirror (111) surfaces with an orientation relationship of (111)[110]BP//(111)[110]Si. At the hetero-interface between the MOCVD-grown BP layer and the Si substrate, an amorphous thin layer containing Si, P, and O (oxygen) was formed. In addition to these features, TED pattern revealed that the BP layer consisted of {111} twins. The MOCVD-grown BP layers showed p-type conductivity with a carrier concentration of $6.3\times10^{19}$ $cm^{-3}$ and with room temperature mobility of 70 $cm^2/Vs$.**

**Key words: Epitaxial growth, Heterostructure, MOCVD, III-V compound semiconductor, Boronphosphide, Si, Twin, Orientation.**

## Introduction

Boronmonophosphide (BP) is known as one of the III-V compound semi-conductors with an indirect band gap of about 2 electron volt (eV) [1-3]. Because of an expedient property to the formation of both of n- and p-conductive layers, BP has been utilized to fabricate Si-based functional semiconductor devices, such as n-BP/p-Si/n-Si npn-heterojunction bipolar transistors (HBT) and Si/BP heterojunction solar cells [4]. Recent research has been also made to grow cubic-gallium nitride (c-GaN)/BP/Si heterostructures utilizing a lower lattice mismatching of c-GaN (lattice constant, $a_0$=0.451 nm) to BP ($a_0$=0.454 nm) [5]. Up to now, the BP semi-conducting layers were grown by various epitaxial growth procedures, such as halide vapor phase epitaxy (VPE) [6, 7], hydride VPE [8], molecular beam deposition [9], etc.. In addition to those procedures, a metalorganic chemical vapor deposition (MOCVD) technique was also employed to grow a BP layer on a Si single crystal substrate [10]. Contrary to the challengeable approach to the formation of Si/BP heterostructures by MOCVD technique, little is known about the crystalline structure of MOCVD-grown BP semiconducting layer hetero-epitaxially stacked on a Si substrate.

In this paper, preliminary crystallographic features of the BP layer directly formed on a Si single crystalline surface are investigated and discussed.

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## Experimental

Silicon (Si) single crystals with (111) orientation were used as substrates. On the mirror-polished (111) surfaces of the substrates, unintentionally-doped BP layers were directly grown utilizing a triethylboran ($(C_2H_5)_3B$)/phosphine ($PH_3$)/hydrogen ($H_2$) MOCVD system. Because the growth temperature which allows epitaxial vapor growth of BP on Si has been reported to be restricted only within 1020°C-1070°C [12], the undoped BP layers were grown at 1025°C under an atmospheric pressure of about $1\times10^5$ Pascal (Pa). The input molar ratio of the $PH_3$ to ($(C_2H_5)_3B$) (=V/III ratio) which was fed to the AIX-200RF (AIXTRON AG, Germany) type horizontal reactor was set to about 150. The flow rate of hydrogen used as the carrier gas to transport the above sources for boron and phosphorous was set to 16 liters/minute. The thickness of the grown BP layer was measured mechanically from cross-sectional SEM photographs for the (110) cleaved surface of the BP layer/Si substrate heterostructure.

The surface state of the grown BP layer was evaluated using a scanning electron microscope (SEM). An X-ray diffraction pattern was taken with a conventional $\theta$-$2\theta$ diffractmeter by using a copper (Cu)K$\alpha$ line with a wavelength of 0.154 nm.

In addition to these measurements, the crystallographic structure inside the BP layer was investigated through a cross-sectional TEM technique. For the cross-sectional TEM observation, the MOCVD-grown BP layer was subjected to mechanical and chemical polishing followed by ion-thinning. An incident electron beam parallel to

the [110] direction of the Si substrate with an acceleration voltage of 200 kV was used in the transmission electron diffraction (TED) observations.

## Results and Discussion

Figure 1 shows an SEM photograph of a continuous film surface of a 450 nm-thick BP layer exhibiting no peeling from the (111)Si substrate surface. Here, the BP layer was grown at a rate of 22.5 nm/minute by setting the input amount of $(C_2H_5)_3B$ to $1.4 \times 10^{-4}$ mol /minute. In spite of a large lattice mismatch of about 16.4% and difference of thermal conductivity between BP and Si, cracks were rarely found in the MOCVD-grown BP as thin as about 450 nm in thickness. Contrary to reddish black BP films grown on fused silica by a $B_2H_6/PH_3$ hydride VPE method [11], the unintentionally-doped BP layers grown by the MOCVD method showed transparency to fluorescent light. Nishinaga have reported that a large amount of stacking faults and anti-phase boundaries makes BP films on (111)Si opaque [12]. As mentioned later, the MOCVD-grown BP layer on the (111)Si substrates actually contains stacking faults and twins. It is not clear at present which parameters affect the transparency of the MOCVD-grown BP layer mostly.

An X-ray diffraction pattern of the BP layers grown on the (111)Si surface at 1020°C is shown in Fig. 2. Diffraction peaks which could be attributed to (111) and (222)BP crystal planes appear in addition to the (222)Si peak from the (111)Si substrate. The origin of a broad diffraction peak at a Bragg angle (=2θ) of around 44° is unclear. Based on the diffraction peak corresponding to (111)BP at a 2θ of 34.1°, the lattice constant of the MOCVD-grown BP layer is calculated from Bragg's law to be 0.454 nm which agrees with the lattice constant of BP reported previously [13, 14].

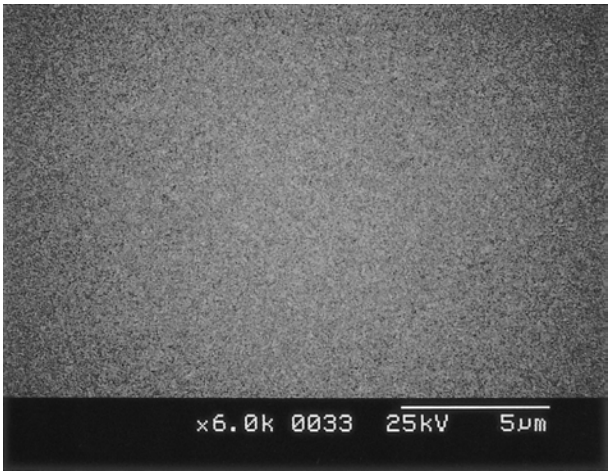


**Fig. 1.** Scanning electron microscopic photograph of a BP surface grown directly on a (111)Si substrate at 1025°C with a $PH_3/(C_2H_5)_3B$ ratio of about 150.

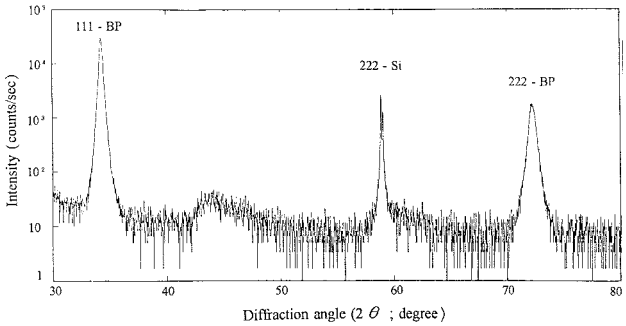


**Fig. 2.** X-ray diffraction pattern of a 450 nm-thick MOCVD-grown BP layer on a (111)Si substrate.

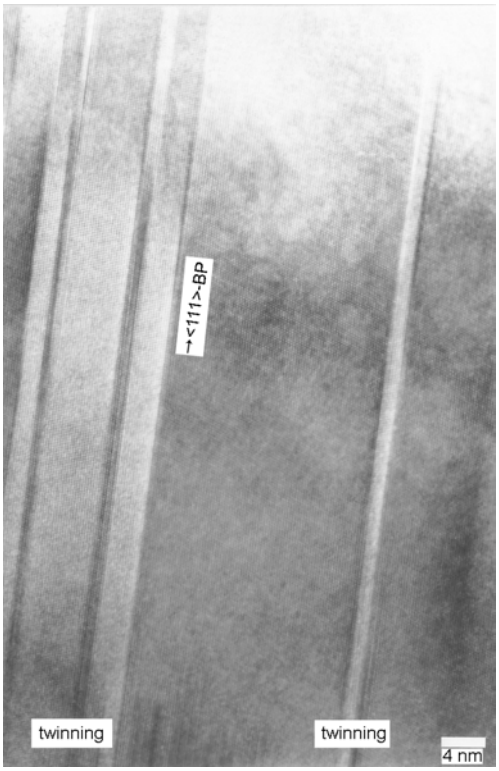


**Fig. 3.** Bright field cross-sectional HRTEM photograph from the BP layer containing {111}-twins.

In addition to the X-ray diffraction measurements, a cross-sectional TEM observation was made to characterize the crystalline structure of the MOCVD-grown BP layer. Voids were merely observed at the hetero-interface between the MOCVD-grown BP layer and the (111)Si substrate. It was, however, recognized that an amorphous thin layer containing Si, P, and O (oxygen) atoms with 6-8 nm in thickness was present at the interface. In addition to this, a lot of twins and stacking faults were observed in the cross-sectional high-resolution TEM (HRTEM) image of the MOCVD-grown BP layer as shown in Fig. 3. The twins are clearly seen to be generated along the <111>BP direction. Figure 4 shows a transmission electron diffraction (TED) pattern of a MOCVD-grown BP layer. For reference, a selected-

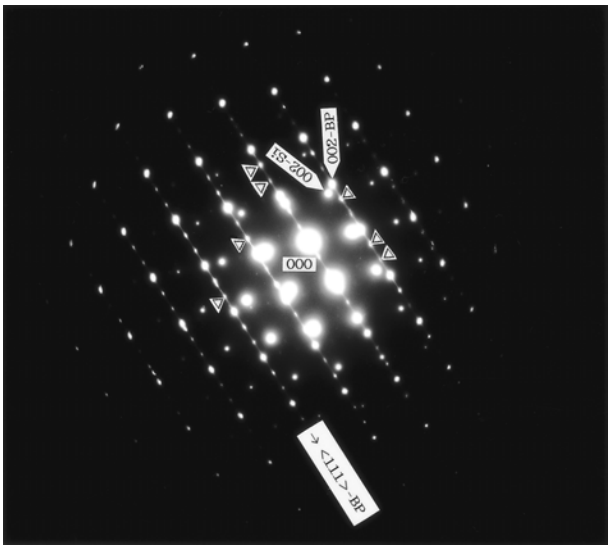


**Fig. 4.** Transmission electron diffraction (TED) pattern from the MOCVD-grown BP layer superimposed by diffraction spots from the (111)Si. Extra spots (Δ) due to the {111}-twins are seen along the <111>BP directions.

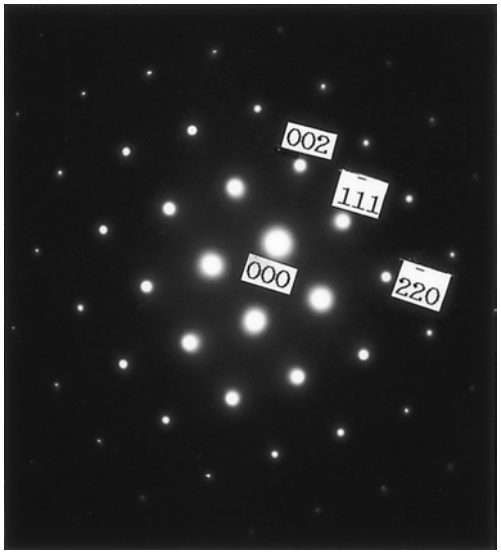


**Fig. 5.** Selected-area TED pattern from the (111)Si substrate with the incident electron beam parallel to the <110> direction. By eliminating spots of the (111)Si from Fig. 4, diffraction spots originating from BP can be distinguished.

area TED pattern from the (111)Si substrate is also given in Fig. 5. The TED pattern was confirmed to be due to superimposed spots from both {111}BP and {111}Si. Because diffraction spots from {111}BP layer were recognized to be arranged along with the [110] Si direction, orientation relationship was confirmed as (111)[110] BP//(111)[110] Si. By comparison of the diffraction spots from the BP (Fig. 4) to the array of spots of the (111)Si (Fig. 5), extra diffraction spots (Δ) could be observed in the TED pattern of the BP layer (Fig. 4). The extra diffraction spots which could be attributed to twins and stacking faults are present in the neighborhood of BP diffraction spots with an interval corresponding to $1/3 \times d_{(111)}$ (where $d_{(111)}$ represents the lattice distance between (111) crystal planes of a BP single crystal). In contrast to this, dislocations penetrating from the (111)Si substrate into the MOCVD-grown BP layer were hardly recognized. This may probably be due to the use of low dislocation density ($<10^2$ cm$^{-2}$) Si single crystal as the substrate.

Hall-effect measurements according to the van der Pauw technique with indium-zinc electrodes showed that the BP layers grown directly on a high-resistance undoped (111)Si substrate ($\rho > 10^3$ Ωcm) had p-type conductivity with a room temperature resistivity (ρ) as low as $1.4 \times 10^{-3}$ Ωcm. A carrier concentration around $6.3 \times 10^{19}$ cm$^{-3}$ was found for the BP layer accompanied with a room temperature mobility of about 70 cm$^2$/Vs. Residual Si impurities are one of the possible acceptors in BP. A quantitative analysis by SIMS (secondary-ion mass spectrometry) revealed, however, that the atomic concentration of Si was below $1 \times 10^{18}$ cm$^{-3}$ in the MOCVD-grown BP layers. This is far less than the carrier concentration mentioned above, even though all of the amphoteric impurities of Si act only as acceptors. The other possible acceptor is a vacancy-related complex formed through an occupation by a group-III boron atom (B) in a vacancy of group-V phosphorous ($V_p$), i.e., B-$V_P$ complex. To ascertain the presence of the B-$V_P$ complex in the MOCVD-grown BP layers, a precise measurement for the lattice constant which is known to change sensitively on alternation of the atomic arrangement of B and P atoms will be, for example, required [15].

## Summary

Boronmonophosphide layers were grown directly on (111)Si by an atmospheric-pressure MOCVD method at 1025ºC. The MOCVD-grown transparent BP layers were made up from (111)BP layers oriented parallel to the (111)Si substrate surface with an epitaxial relationship of (111)[110]BP //(111)[110]Si. The MOCVD-grown BP layers were characterized by the presence of {111}-twins and stacking faults. Furthermore, the MOCVD-grown BP layers matched well in lattice constant to that of c-GaN and could be grown with free from cracks on the (111)Si substrates.

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