PREPARATION, PROPERTIES, AND CHARACTERIZATION OF BORON PHOSPHIDE FILMS ON 4H- AND 6H-SILICON CARBIDE

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Abstract

Epitaxial growth of boron phosphide (BP) films on 4H- and 6H-SiC(0001) substrates with on- and off-axis orientations was investigated in this study. The films were prepared by chemical vapor deposition using phosphine and diborane as reactants over a temperature range of 1000°C-1200°C. The effects of growth parameters such as temperature, reactant flow rates, substrate type, and crystallographic orientation on BP film properties were studied in detail. The epitaxial relationship between BP film and 4H- and 6H-SiC substrate was (111)BP <112>BP || (0001)SiC <110>SiC. Film quality, determined by preferred crystalline orientation and grain size, improved with temperature and PH₃/B₂H₆ flow ratio, as indicated by scanning electron microscopy, x-ray diffraction, atomic force microscopy and Raman spectroscopy. In addition, smoother films were obtained when the diborane flow rate was reduced. Rotational twinning in BP films was absent on 4H-SiC(0001) tilted 4° towards [1100], but was confirmed on both 4H-SiC(0001) tilted 4° towards [1210], and on-axis 6H-SiC(0001) substrates by synchrotron white beam x-ray topography technique.

1. Introduction

Among all the boron compound semiconductors, cubic boron phosphide (BP) has the greatest potential for electronic devices due to its proven ability to have both *n*- and *p*-type conductivities, high thermal conductivity, and wide energy bandgap (2.0 eV). In addition to BP's unique properties, the ¹⁰B isotope has a large thermal neutron capture cross section that is attractive for solid state neutron detectors¹. In order for a neutron detection device to be effective and efficient, BP should have low dislocation densities and low residual (unintentional) impurities. Most previous studies on heteroepitaxial growth of BP films have reported significant amounts of residual impurities and defect densities, thereby resulting in poor electrical properties. These can be attributed to the choice of substrate and growth conditions employed. Although silicon (Si) and sapphire have been the most studied substrates, they have significant disadvantages of large lattice constant and coefficient of thermal expansion mismatches.² Previous studies have reported very high (10¹⁸ to 10²⁰ cm⁻³) unintentional Si concentrations in BP films on silicon substrates due to Si diffusion and autodoping.³⁻⁷ Furthermore, the thermal instability of silicon limits the maximum temperature to less than 1050°C for its use as a substrate; at higher temperatures, Si incorporation makes it difficult to control the BP's electrical properties.

In this study, silicon carbide (SiC) was explored as a potential substrate to improve BP epitaxial film properties. SiC demonstrates a smaller lattice constant mismatch (-4.2%) with BP than Si and sapphire, has a nearly identical coefficient of thermal expansion² to that of BP, and is much more inert than Si. In addition, SiC has better thermal stability than Si at high temperatures, thereby decreasing the possibility of autodoping from the substrate. However, due to the mismatch of crystal symmetries between BP (three-fold symmetry) and 4H- and 6H-SiC (six-fold symmetry), rotational twinning may occur. Previous studies on BP/SiC have reported the existence of stacking faults and rotational twinning.^{8,9} Zhang *et al*¹⁰ reported that use of 4H-

SiC(0001) substrates tilted towards the [1100] direction could eliminate twinning in icosahedral boron arsenide ($B_{12}As_2$) epitaxial films. Here, we investigate the BP film growth on intentionally misoriented 4H-SiC(0001) and 6H-SiC(0001) substrates in order to eliminate rotational twinning.

2. Materials and methods

Boron phosphide (BP) films were deposited by chemical vapor deposition (CVD) using ultra-high purity phosphine (99.999% PH_3) and diborane (1% B_2H_6 in H_2) as reactant gases and palladium membrane purified hydrogen as carrier gas. The CVD reactor consisted of a horizontal quartz tube cooled externally by a water jacket. Substrates were cleaned using conventional techniques prior to heating on a TaC coated graphite susceptor with RF induction. Temperature of the samples was accurately measured by calibrating the thermocouple against the melting of a silicon piece on the susceptor. BP films were deposited on a variety of 4H- and 6H-SiC substrates: Si-face 4H-SiC(0001) tilted 4° towards [1100], Si-face 4H-SiC(0001) tilted 4° towards [1210], Si-face 6H-SiC(0001) tilted 3.5° towards [1210], Si-face on-axis 6H-SiC(0001), and C-face 4H-SiC(0001) tilted 4° towards [1100].

Substrates were subjected to *in situ* hydrogen etching at $1650^\circ C$ for approximately 15 min prior to BP deposition in order to produce atomically flat terraces on the substrate surface¹¹. BP films were characterized at three temperatures ($1000^\circ C$, $1100^\circ C$, and $1200^\circ C$); for each temperature, three PH_3/B_2H_6 (1% in H_2) flow rate ratios (40/40 sccm, 40/26.6 sccm, and 40/20 sccm respectively) were maintained. The effect of reactant flow rates on crystal quality was analyzed by changing the diborane flow rates and keeping constant phosphine flow rates at each temperature ($1000^\circ C$, $1100^\circ C$ and $1200^\circ C$). All depositions were performed at near atmospheric pressure (700 torr). Temperature, flow rate of reactant gases, substrate type, and misorientation strongly influenced morphology, crystal orientation, and film quality.

Surface morphology, grain size, and surface roughness of the films were analyzed by scanning electron microscopy and atomic force microscopy. Crystalline quality of the films and epitaxial relationship between the grown films and the substrate was determined by x-ray diffraction, synchrotron white beam x-ray topography (SWBXRT) and Raman spectroscopy. Rotational twinning and residual stress in the BP films were analyzed using SWBXRT technique.

3. Results and discussion

BP films were deposited on Si- and C-face SiC(0001) substrates at similar conditions and crystalline quality was compared in order to study the effect of substrate polarity. No significant difference in crystalline orientation of BP(111) plane on Si- and C-face 4H-SiC(0001) substrates was observed; however, films deposited on C-face substrate had rougher surfaces than Si-face due to the deep etch pits generated by *in situ* hydrogen etching. X-ray topography analysis showed large strain in the BP film deposited on C-face 4H-SiC(0001) substrate compared to the Si-face 4H- and 6H-SiC(0001) substrates. Therefore, growth on Si-face 4H- and 6H-SiC(0001) substrates became the focus of this study. BP films deposited on 4H-SiC(0001) substrates were highly oriented and had better crystalline quality compared to 6H-SiC(0001) substrates, due in part to the lower quality of 6H-SiC compared to 4H-SiC substrate. Therefore, a majority of films were deposited on 4H-SiC(0001) tilted 4° towards [1100] and 4° towards [1210].

3.1 Effect of temperature

Morphologies of films grown at three temperatures ($1000^\circ C$, $1100^\circ C$, and $1200^\circ C$) on a Si-face 4H-SiC(0001) tilted 4° towards [1210] substrate are shown in Figure 1. Films deposited at $1000^\circ C$ had small grains with no geometrical features or specific crystalline orientation. At $1100^\circ C$, grain size was larger and crystallites appeared to have triangular features oriented in a specific direction. At $1200^\circ C$, crystallites had regular three-fold symmetric triangular features, and individual small grains merged to form a larger grain with preferred crystalline orientation. At higher temperatures ($1200^\circ C$), adatoms were more mobile and incorporated preferably at step

edges instead of terraces on the substrate surface, resulting in controlled nucleation. Hence, epitaxial film growth occurred because of the advancement of steps along the terraces, which is typical of a step flow growth mode. A similar trend in crystalline orientation and grain size was observed for BP films grown on Si-face 4H-SiC(0001) tilted 4° towards [1100] under similar reaction conditions. In general, growth rate at 1200°C was approximately 5-6 µm/hr.

3.2 Effect of reactant flow rates

Excess phosphine was used to maintain a high phosphorus vapor pressure in order to prevent decomposition of BP to B₁₂P₂. Consequently, the deposition rate was limited by the diborane flow rate. Initial depositions were performed at 1150°C with gas flow rates of 3500 sccm H₂, 80 sccm PH₃ and 80 sccm B₂H₆ (1% in H₂). These films had rough surfaces with a large number of spheres (or ballas) on the surface due to high supersaturation and rapid deposition of reactant materials on the surface. When PH₃ and B₂H₆ (1% in H₂) flow rates were reduced below 30 sccm and 20-30 sccm respectively to control the deposition rate, thin, non-uniform and polycrystalline BP films were achieved. Reactant flow rates were subsequently tuned to control the growth rate and to obtain smooth, single crystalline films. Optimum flow rates at temperatures of 1000°C and 1150°C were determined to be 4000 sccm H₂, 30-40 sccm PH₃ and 30-40 sccm B₂H₆ (1% in H₂). Temperatures above 1150°C required the phosphine flow rate to be increased in order to maintain phosphorus vapor pressure because phosphorus decomposition pressure increases exponentially with temperature. Flow rates optimized at 1200°C were 4000 sccm H₂, 40-80 sccm PH₃ and 40-80 sccm B₂H₆ (1% in H₂).

Figure 2 shows SEM micrographs of films deposited at 1200°C for three diborane flow rates. At a given temperature, for example 1200°C, when the diborane flow rate decreased, i.e. increased PH₃/B₂H₆ ratio, the crystallites became more textured and the surfaces were smoother than the films deposited at lower PH₃/B₂H₆ ratio. There was no significant change in the crystalline orientation of the films but the surface roughness decreased with decreasing diborane flow rate, possibly due to a reduced deposition rate.

AFM was employed to measure RMS roughness of BP films grown at various reaction conditions shown in Table 1. RMS roughness of BP films decreased with increasing the PH₃/B₂H₆ ratio and the magnitude of decrease in roughness was highest at 1200°C. At a given PH₃/B₂H₆ ratio (for example PH₃/B₂H₆ =100), surface roughness increased with temperature, perhaps due to increase in reaction rate resulting in thicker films. Figure 3 shows the AFM images taken over a range of 30x30 µm² of BP films deposited at three temperatures. The grain size increased with temperature at a constant reactant flow rates, and when the PH₃/B₂H₆ ratio was increased at a constant temperature.

3.3 X-Ray topography analysis

Synchrotron white beam x-ray topographs (SWBXT) were taken on BP films deposited on three types of substrates: 4H-SiC(0001) tilted 4° towards [1100], 4H-SiC(0001) tilted 4° towards [1210], and on-axis 6H-SiC(0001). Diffraction spots from BP(111) on the 4H-SiC miscut towards [1100] had a single rotational orientation. They were also well-defined and free from long range and inhomogeneous strains (Figure 4(a)). In this case, two types of steps were formed on the SiC substrate during the H₂ etching; zinc-blende steps exhibiting single dangling bonds, and wurtzitic steps exhibiting double dangling bonds.¹⁰ During epitaxy, BP crystallites preferentially nucleated at the lower energy zinc-blende step and bonded to a terrace and vertical step riser on which only one orientation of BP can nucleate, thereby eliminating rotational twinning. In contrast, for BP on SiC miscut towards [1210], diffraction spots revealed that the BP(111) had two orientations (rotational twins). The spots also were slightly elongated, indicating that the films were strained (Figure 4(b)). For on-axis 6H-SiC, BP(111) was twinned and the spots were more elongated compared to the other two substrates, indicating residual stress in the film (Figure 4(c)). The orientation relationship between BP film and 4H- and 6H-SiC(0001) substrate was (111) <112> || (0001) <1 100>. In Figure 4, BP (cubic crystal structure) diffraction spots are shown in Miller indices whereas SiC (hexagonal crystal structure) spots are shown in Miller-Bravais indices.

3.4 X-Ray diffraction analysis

The XRD pattern of BP film deposited on a 4H-SiC(0001) substrate at 1000°C and $\text{PH}_3/\text{B}_2\text{H}_6=200$ is shown in Figure 5, with major BP(111) orientation and all other possible BP orientations. Along with major BP(111) peak, weak intensity peaks from BP(200) and BP(220) orientations were also frequently observed. In this study, crystallinity of BP films was described by relative intensity ratios of XRD peaks, expected to approach infinity for single crystals. The major BP(111) peak intensity and ratio of peak intensities from BP(111) to BP(200) and BP(220) orientations were specifically compared.

XRD data of films grown at various temperatures (1000°C, 1100°C, and 1200°C) with three $\text{PH}_3/\text{B}_2\text{H}_6$ ratios (100, 150 and 200) were plotted as shown in Figure 6. In general, BP(111) peak intensity increased with temperature at a fixed $\text{PH}_3/\text{B}_2\text{H}_6$ flow ratios (150 and 200), with the exception for the curve $\text{PH}_3/\text{B}_2\text{H}_6=100$. The increase in peak intensity was moderate at 1100°C for all three $\text{PH}_3/\text{B}_2\text{H}_6$ ratio curves, but the steepest increase was observed at 1200°C for the curve $\text{PH}_3/\text{B}_2\text{H}_6=200$. This increase may partially be attributed to increase in film thickness at higher temperatures because of increased reaction rate. Relative peak intensity ratios of BP(111)/BP(200) and BP(111)/BP(220) demonstrated a similar trend with changes in temperature and $\text{PH}_3/\text{B}_2\text{H}_6$ ratios, as shown in Figure 6(b) and (c). These ratios increased with temperature for any $\text{PH}_3/\text{B}_2\text{H}_6$ ratio in most cases, most steeply for films grown at 1200°C and $\text{PH}_3/\text{B}_2\text{H}_6=200$. The highest peak intensity ratios for BP(111)/BP(200) was 1651 and for BP(111)/BP(220) was 499, the highest ever reported in the literature.

Full width at half maximum (FWHM) of the BP(111) peak extracted from the 2θ scans for the films deposited on 4H-SiC(0001) 4° miscut towards [1100] and [1210] directions at various reaction conditions are shown in Figures 7(a) and (b). In both cases, FWHM sharply decreased as the temperature increased from 1000°C to 1100°C for the curve $\text{PH}_3/\text{B}_2\text{H}_6=100$, while the decrease was moderate for the other two. The peak width was narrowest at 1200°C for all these three $\text{PH}_3/\text{B}_2\text{H}_6$ curves. The lowest value of FWHM was 0.19° for film deposited at 1200°C at $\text{PH}_3/\text{B}_2\text{H}_6=200$ on 4H-SiC(0001) 4° miscut towards [1210] direction. Therefore, XRD analysis led to the conclusion that the highest and steepest increase in BP(111) peak intensity, highest relative peak height ratios and narrowest BP(111) peak widths indicate that crystalline quality of the films improved by increasing the deposition temperature and increasing the $\text{PH}_3/\text{B}_2\text{H}_6$ ratio. This conclusion suggests that higher temperature and reduced diborane flow rate will enable controlled nucleation at the step edges and improve crystalline orientation of incoming adatoms.

3.5 Raman spectroscopy analysis

Raman spectra of BP films grown on 4H-SiC substrate tilted 4° towards [1210] direction at three temperatures is shown in Figure 8. The spectra exhibited two bands: a weak transverse-optical (TO) phonon mode around 794 cm^{-1} and a strong longitudinal-optical (LO) phonon mode around 824-827 cm^{-1} . Peaks at 776 cm^{-1} and 964 cm^{-1} corresponded to TO and LO phonon modes of 4H-SiC(0001) substrate. These phonon mode values are in agreement with values reported in the literature.^{3,12,13} BP peak position shifted to the lower value when the temperature increased from 1000°C to 1200°C. Also, resolution of the weak TO band that appeared at approximately 794 cm^{-1} improved when the temperature increased. Raman spectra taken on each sample having an area of 10x10 mm² at various locations showed more or less similar values of phonon modes indicating that the films are homogeneous. No additional peaks associated with the presence of icosahedral boron phosphide ($\text{B}_{12}\text{P}_{12}$), which typically forms at higher temperatures, were evident.

FWHM values of the LO phonon mode of BP deposited on 4H-SiC(0001) 4° miscut towards [1210] direction are shown in Table 2. Peak widths narrowed with temperature at a fixed $\text{PH}_3/\text{B}_2\text{H}_6$ ratio (for example $\text{PH}_3/\text{B}_2\text{H}_6=100$), and with increased $\text{PH}_3/\text{B}_2\text{H}_6$ ratio (reduced diborane flow rate) at a given temperature. When the FWHM values at 1000°C, 1100°C and 1200°C are compared at each $\text{PH}_3/\text{B}_2\text{H}_6$ ratio (100,150 and 200), the extent of decrease in peak width with temperature is more notable at 1200°C, suggesting that higher temperatures enabled better crystalline quality. The lowest FWHM value obtained was 9.5 cm^{-1} at 1200°C and

PH₃/B₂H₆ ratios of 150 and 200. Narrow peak widths with similar Raman spectra at various locations on samples show the films were uniform with good crystalline quality.

4. Conclusions

Single crystalline BP films with high structural quality were successfully grown on 4H- and 6H-SiC(0001) substrates. The crystalline quality of BP films as determined by surface morphology, grain size, Raman spectra, and XRD improved with temperature, and reduced diborane flowrate. The best structural quality was achieved at a deposition temperature of 1200°C with a PH₃/B₂H₆ flow rate ratio of 200. The best substrate choice for BP epitaxy was 4H-SiC(0001) miscut 4° towards [1210] direction because it did not produce rotational twins defects.

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Figures

Fig 1. SEM micrographs of BP films deposited on Si-face 4H-SiC(0001) tilted 4° towards [1210] at temperatures (a) 1000°C, (b) 1100°C, and (c) 1200°C

Fig 2. SEM micrographs of the surface features of BP films deposited on 4H-SiC(0001) tilted 4° towards [1210] at 1200°C with $\text{PH}_3/\text{B}_2\text{H}_6$ flow ratio of (a) 100, (b) 150, and (c) 200

Fig 3. AFM images of BP films grown on 4H-SiC(0001) tilted 4° towards [1100] at $\text{PH}_3/\text{B}_2\text{H}_6=200$ and at temperatures of (a) 1000°C (b) 1100°C , and (c) 1200°C .

Fig 4. Transmission X-ray topographs of BP films on (a) 4H-SiC 4° miscut towards [1100], (b) 4H-SiC 4° miscut towards [1210], and (c) on-axis 6H-SiC substrate. Diffraction spots marked with red circles indicate the substrate, violet triangles indicate BP (111) plane and black rectangles indicate BP (111) twins.

Fig 5. Log intensity XRD pattern with peaks from the minor, misoriented planes of BP, deposited on a 4H-SiC(0001) substrate 4° tilt towards [1100] at 1000°C and $\text{PH}_3/\text{B}_2\text{H}_6=200$.

Fig 6. (a) BP(111) peak intensity and peak intensity ratios of (b) BP(111)/BP(200), and (c) BP(111)/BP(220) orientations obtained from XRD of BP films grown on 4H-SiC(0001) 4° miscut towards [1100].

Fig 7. FWHM curves of BP(111) peak obtained from 2 scans of the films grown at various reaction conditions. BP films were deposited on 4H-SiC(0001) 4° miscut towards (a) [1100], and (b) [1210] directions.

Fig 8. Raman spectra obtained from BP films deposited on 4H-SiC(0001) 4° miscut towards [1210] directions at $\text{PH}_3/\text{B}_2\text{H}_6=200$.

TABLES

Table 1. RMS roughness values of BP films grown on 4H-SiC(0001) 4° miscut towards [1210] measured by AFM

Temp (°C)	Roughness RMS (nm)		
	$\text{PH}_3/\text{B}_2\text{H}_6=100$	$\text{PH}_3/\text{B}_2\text{H}_6=150$	$\text{PH}_3/\text{B}_2\text{H}_6=200$
1000	34	34	30
1100	62	49	47
1200	102	85	74

Table 2. Raman FWHM values for the BP (LO) mode at various reaction conditions.

Temp (°C)	FWHM (cm^{-1})		
	$\text{PH}_3/\text{B}_2\text{H}_6=100$	$\text{PH}_3/\text{B}_2\text{H}_6=150$	$\text{PH}_3/\text{B}_2\text{H}_6=200$
1000	14.7	13.8	12.3
1100	11.7	11.3	11.3
1200	10.1	9.5	9.5