CVD Growth and Properties of Boron Phosphide on 3C-SiC

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ABSTRACT

Improving the crystalline quality of boron phosphide (BP) is essential for realizing its full potential in semiconductor device applications. In this study, 3C-SiC was tested as a substrate for BP epitaxy. BP films were grown on 3C-SiC(100)/Si, 3C-SiC(111)/Si, and 3C-SiC(111)/4H-SiC(0001) substrates in a horizontal chemical vapor deposition (CVD) system. Films were produced with good crystalline orientation and morphological features in the temperature range of 1000 to 1200 °C using a $\text{PH}_3 + \text{B}_2\text{H}_6 + \text{H}_2$ mixture. Rotational twinning was absent in the BP due to the crystal symmetry-matching with 3C-SiC. Confocal 3D Raman imaging of BP films revealed primarily uniform peak shift and peak widths across the scanned area, except at defects on the surface. Synchrotron white beam X-ray topography showed the epitaxial relationship between BP and 3C-SiC was $(100) \langle 011 \rangle_{\text{BP}} \parallel (100) \langle 011 \rangle_{3\text{C-SiC}}$ and $(111) \langle 11\bar{2} \rangle_{\text{BP}} \parallel (111) \langle 11\bar{2} \rangle_{3\text{C-SiC}}$. Scanning electron microscopy, Raman spectroscopy and X-ray diffraction analysis indicated residual tensile strain in the films and improved crystalline quality at temperatures below 1200 °C. These results indicated that BP properties could be further enhanced by employing high quality bulk 3C-SiC or 3C-SiC epilayers on 4H-SiC substrates.

Keywords: B2.Semiconducting III-V materials, A3.Hydride vapor phase epitaxy, A1.Characterization, A1.High resolution X-ray diffraction, A1.X-ray topography, A1.Defects.

1. INTRODUCTION

Boron phosphide (BP) is an indirect wide-bandgap (2.0 eV) semiconductor with many outstanding properties making it attractive for various electronic device applications such as solid-state neutron detectors.[1] Bulk crystals of BP are not readily available, thus its films must be deposited on foreign substrates. In heteroepitaxy, the choice of substrate influences the morphology, crystal orientation, defect densities, impurities, and residual strain of the epitaxial layers. BP epitaxy on Si and sapphire substrates was extensively studied more than 20 years ago, but these substrates produced BP films with high concentrations of unintentional impurities and structural defects limiting its applications in electronic devices.[2–6] Other substrates are now available that may produce superior quality BP films such as SiC (4H, 6H and 3C), AlN, and ZrB_2 . These materials offer better matches of lattice constants and coefficients of thermal expansion with BP, in addition to higher chemical and thermal stability compared to Si and sapphire.

3C-SiC is the most attractive SiC polytype as a substrate for BP epitaxy since both materials have the zinc-blende structure. Due to their matching crystal symmetry, 3C-SiC has the potential to eliminate in-plane rotational twinning in BP films and variations in stacking sequence at the interface. Generation of rotational twin defects are common when the substrate material has a higher symmetry than the epilayer crystal. For example, BP(111) rotational twin defects were observed when deposited

on hexagonal substrates such as 4H-SiC(0001) and AlN(0001).[7–13] BP(111) had an index of symmetry of three whereas the (0001) plane of hexagonal substrates had an index of symmetry of six. This difference in crystal symmetry allowed two orientations of BP(111) that are related by a rotation of 180° to be deposited on the (0001) plane, leading to rotational twinning. These defects significantly contribute to the modification of electrical properties of BP, such as lifetime of minority carriers and carrier mobility. Other appealing properties of 3C-SiC as a substrate include its high thermal stability, small lattice constant mismatch (4.1%), and nearly identical coefficients of thermal expansion with BP.[14,15] 3C-SiC has a wide bandgap (2.2 eV) and high electron mobility of $\sim 900 \text{ cm}^2/\text{V}\cdot\text{s}$,[16] making it suitable for heterojunction devices with BP.

Bulk 3C-SiC single crystals with large surface areas would be ideal for growing BP films, but they are not widely available. However, large area 3C-SiC epitaxial films on silicon substrates are commercially available. These substrates are relatively inexpensive, and are available in different orientations. Past studies have shown Si contamination in BP films deposited directly on Si via autodoping and diffusion of Si atoms from Si substrate into the BP films.[1–5] Si contamination could possibly be minimized using a 3C-SiC epilayer on Si since the diffusion of Si atoms in SiC is very low at typical BP deposition temperatures.[17] Furthermore, 3C-SiC on 4H-SiC(0001) have been produced by Jokubavicius et al[18,19]. Such substrates can minimize Si contamination prevalent with Si substrates. 3C-SiC/4H-SiC substrates have an additional advantage of enabling the deposition of BP at much higher temperatures compared to 3C-SiC/Si due to the enhanced thermal stability of 3C-SiC on 4H-SiC over Si. There are only a few prior reports of BP epitaxy on 3C-SiC in the literature. Li[20] investigated the growth of BP films on a 3C-SiC template, but epitaxy was not achieved; the film was a mixture of amorphous and polycrystalline BP. Li attributed it to the poor quality of initial 3C-SiC epilayer which was thin and non-uniform.

The present study investigated 3C-SiC templates as substrates for growing BP films over a wide range of process parameters. This paper describes the CVD growth and a detailed characterization of BP films grown on various orientations and types of 3C-SiC substrates. The effects of process variables such as temperature and reactant flow rates on the morphology, crystalline quality, residual strain and defects in the films are reported in detail.

2. EXPERIMENTAL

BP films were synthesized in a horizontal CVD reactor using ultra-high purity phosphine (99.999%) and diborane (1% in H_2) gases as phosphorus and boron precursors. The carrier gas was ultra-high purity hydrogen. Details of the CVD set-up were described in our previous work.[8,10,12,21] Three types of substrates were employed for BP deposition: 3C-SiC(100) on Si(100), 3C-SiC(111) on Si(111), and 3C-SiC(111) on 4H-SiC(0001). The 3C-SiC films on Si were polished to minimize their surface roughness before BP epitaxy. The 3C-SiC(100) films had a thickness of $\sim 4 \text{ }\mu\text{m}$, total thickness variation of $3 \text{ }\mu\text{m}$ and wafer bow of $6 \text{ }\mu\text{m}$ over a 4-inch Si(100) wafer, while 3C-SiC(111) films had a thickness of $\sim 0.9 \text{ }\mu\text{m}$, total thickness variation of $13 \text{ }\mu\text{m}$ and wafer bow of $-43 \text{ }\mu\text{m}$ over a 4-inch Si(111) wafer. The 3C-SiC(111) templates on 4H-SiC(0001) were not polished and had a thickness of about $50 \text{ }\mu\text{m}$. The hydrogen flow rate was kept constant at 4,000 sccm, and the PH_3 and B_2H_6 (1% in H_2) flow rates were varied between 30-80 sccm and 20-80 sccm, respectively. The deposition temperature was varied between 1000 to 1200 $^\circ\text{C}$ over a period of 30 min to 3 h. A constant pressure of 700 torr was maintained inside the reactor chamber for all depositions.

The surface morphology of the films was characterized by scanning electron microscopy (SEM) using an FEI Versa 3D DualBeam microscope. Crystal quality of the films was analyzed by 3D Raman mapping using an Alpha300 AR+ confocal Raman imaging system (WITec Instruments Corp.) equipped with a UHTS300 spectrometer, DV970 EMCCD camera and 532 nm frequency-doubled Nd:YAG laser as an excitation light source. 3D Raman images were acquired and analyzed using WITecControl and WITecProject Plus softwares, respectively. X-ray diffraction $\theta/2\theta$ scans were performed using a Rigaku Miniflex II desktop X-ray diffractometer with $\text{CuK}\alpha_1$ (1.54 Å) radiation to assess the crystalline orientation of BP. High-resolution X-ray diffraction (HRXRD) double axis rocking curve scans (ω and $\omega-2\theta$) were recorded to evaluate crystalline quality and lattice strain in the BP films. The HRXRD system was equipped with a Bede D1 diffractometer with $\text{CuK}\alpha_1$ (1.54 Å) radiation; beam conditioning was performed using Max-Flux optics and a Ge (111) monochromator. Synchrotron white beam X-ray topography (SWBXT) was used to look for rotational twinning in BP. The white beam radiation was irradiated parallel to the [100] and [111] directions of the 3C-SiC/Si substrates.

3. RESULTS AND DISCUSSION

Figure 1: Indexed transmission X-ray topographs recorded on (a) 3C-SiC(100)/Si and (b) 3C-SiC(111)/Si. Spots indicated by circles represent overlapped diffraction spots from BP, 3C-SiC and Si.

Evidence of rotational twinning in BP films and the epitaxial relationship between BP and 3C-SiC/Si substrates were analyzed using SWBXT. Figures 1a and b display the 4-fold and 3-fold diffraction patterns obtained from BP films grown on 3C-SiC(100)/Si and 3C-SiC(111)/Si substrates, respectively. Diffraction spots from the zinc-blende structural layers of BP and 3C-SiC overlap completely and partially with diamond structure of Si, confirming that BP layers were epitaxially grown on both substrates. The epitaxial relationship between BP and 3C-SiC was $(100) \langle 011 \rangle_{\text{BP}} \parallel (100) \langle 011 \rangle_{\text{3C-SiC}}$ and $(111) \langle 11\bar{2} \rangle_{\text{BP}} \parallel (111) \langle 11\bar{2} \rangle_{\text{3C-SiC}}$. Also, absence of diffraction spots from the twin orientations of BP(100) and BP(111) on 3C-SiC(100) and 3C-SiC(111) substrates, respectively, confirmed that rotational twinning was eliminated. This was due to crystal symmetry matching between BP and 3C-SiC at the interface as both have same zinc-blende crystal structure. The Laue diffraction patterns recorded for BP on both 3C-SiC substrates were compared to simulated patterns to

evaluate strain in the films. Diffraction spots from BP were highly elongated, confirming high residual strain in BP compared to well-defined spots from the relatively low strain 3C-SiC and high quality Si substrate. BP films deposited on 3C-SiC(111)/Si were more strained than on 3C-SiC(100)/Si, as the diffraction spots were more highly elongated.

3C-SiC epilayers were expected to have significant residual strain due to large lattice and thermal expansion mismatches between 3C-SiC and Si.[14,15] Because the 3C-SiC films on Si were already strained, the BP films were also expected to be strained. Confocal Raman imaging was employed to examine the residual strain and overall quality of the BP films. Raman spectra measured from BP films grown on various 3C-SiC epilayers generally gave two characteristic phonon modes: TO mode at $\sim 798 \text{ cm}^{-1}$ and LO mode at $\sim 828 \text{ cm}^{-1}$. The measured peak positions of both phonon modes were in good agreement with the previously published data.[2,8,10,12,21,22] However, the Raman peaks position varied with the substrate used for BP epitaxy due to residual compressive or tensile strain generated in the films.

Figure 2: Raman images recorded on BP/3C-SiC(100)/Si at room temperature over an area of $10 \mu\text{m} \times 10 \mu\text{m}$ with 532 nm excitation. (a) Map of BP(LO) mode peak shift from center position; (b) Map of BP(LO) mode peak width (FWHM). Units are in cm^{-1} .

Raman spectra were collected at 10,000 points over an area of $10 \mu\text{m} \times 10 \mu\text{m}$ on BP film grown on a 3C-SiC(100)/Si substrate at 1000°C . All data points were mapped in a 3D plot with respect to their BP(LO) phonon's peak shift from the center position and peak width (full width at half maximum) as shown in Figures 2a and b. The peak shift from the center position is mostly uniform over the scanned area, except at a few places where deep valleys were present (indicated in numbers from 1 to 5). The peak position across these five valleys was about 824.5 cm^{-1} while the average value across the entire scanned area was 828.7 cm^{-1} . This sharp decrease in peak position in the valleys compared to the surrounding areas or average value indicated local tensile strain in the BP film. Strain in the BP crystal causes structural disorder and can change equilibrium positions of atoms in crystal lattice. Consequently, the phonon frequencies from the film shift to either higher or lower wavenumbers depending on local deformation in the lattice, in this case to the lower side in the valleys. The peak positions at the deepest and highest points were 824.5 cm^{-1} and 830.5 cm^{-1} and the

overall standard deviation in peak shift was 0.50 cm^{-1} . The Raman map of full width at half maximum (FWHM) was also mostly uniform over the scanned area except at some locations where high peaks (numbered from 1 to 5 in Figure 2b) were present. The average FWHM value across the scanned area was 6.9 cm^{-1} while it sharply increased to 18.2 cm^{-1} at the peaks. The locations of these peaks were the same as observed for the valleys in peak shift image, suggesting that crystal quality has degraded at locations where tensile strain was present. The FWHM values at the deepest and highest points were 20.5 cm^{-1} and 11.4 cm^{-1} while a high overall standard deviation of 1.65 cm^{-1} was measured due to high values of FWHM at peaks.

An optical image of BP film analyzed for Raman imaging is shown in Figure 3a along with the scanned area. A closer look at the surface features of BP film in the scanned region and Raman shift image (Figure 2a) indicated that valleys in Raman shift image appeared at locations where huge pits (indicated in numbers) were present on the BP film in Figure 3a. Several possible causes of these pits were considered including the natural surface roughness of the BP film, the presence of pinhole/step bunch defects in 3C-SiC epilayer before BP deposition, defects formed in SiC films during BP epitaxy, or a combination of these phenomena. For more insights, the surface of a bare 3C-SiC(100) epilayer was studied by optical microscopy. Several pinholes were clearly observed on the surface, as shown in Figure 3b. Furthermore, these pinholes remain even after the BP film was deposited on 3C-SiC(100)/Si substrate as shown in Figures 3c and d. A detailed structural characterization of these films would provide more explanation of the defects, but that characterization is beyond the scope of the present work. In summary, the significant shift in Raman peak position around the defects, which indicated strain in the BP film, could be due to a combination of factors.

Figure 3: (a) Optical image of the BP film and scanned area (shown in box) with Raman imaging. (b) Nomarski image of bare 3C-SiC substrate showing pinholes on surface. (c, d) SEM images of BP film deposited on pinholes on 3C-

Figure 4: Comparison of Raman peak positions of BP deposited on various 3C-SiC layers to strain-free BP whiskers.

The average LO phonon peak positions of BP grown on 3C-SiC(100)/Si, 3C-SiC(111)/Si, and 3C-SiC(100)/4H-SiC(0001) at 1200 °C were measured and compared with the peak positions of BP whiskers. The BP whiskers were grown on a 4H-SiC(0001) substrate at 1200 °C via VLS mechanism using Cr metal catalyst. BP whiskers were expected to be strain-free since these crystals freely grow outward off the substrate relaxing the strain unlike an epitaxial film, which is constrained by the substrate. The peak positions of BP films on all 3C-SiC layers were consistently lower than that of strain-free BP whiskers as shown in Figure 4. The lower shift in peak position indicated tensile strain in the BP films on 3C-SiC layers. This conclusion is consistent with the thermal expansion coefficients of BP and 3C-SiC published in the literature, which support that thermal expansion between BP and SiC produce tensile strain.[14,15,23] Furthermore, the peak positions were very close between 3C-SiC/Si and 3C-SiC/4H-SiC, which indicates that thermal expansion of Si had a minor role to play during BP growth. It can be concluded that the shift was due to a combination of tensile strain from thermal expansion mismatch between BP and 3C-SiC and intrinsic strain in the BP film during growth. Also, BP grown on 3C-SiC(111)/Si had a slightly longer shift ($\sim 2 \text{ cm}^{-1}$) compared to other two substrates revealing larger intrinsic strain. Hence, it is crucial to use high quality 3C-SiC to improve the quality and overall properties of BP. The peak positions also shifted to lower wavenumbers when growth temperatures increased for a given substrate, due to increased tensile strain in the film at higher temperatures. This is consistent with the trend for BP films deposited on 4H-SiC reported in our previous work.[10] It suggests that the coefficients of thermal expansion of substrates considered in this study are less than that of BP.

Figure 5: SEM pictures of BP films deposited on 3C-SiC(100)/Si (a, b and c) and 3C-SiC(111)/Si (d, e and f) at 1000 °C, 1100 °C, and 1200 °C.

The surface morphology of BP films deposited at various deposition conditions was analyzed by SEM and Nomarski optical microscopy (DIC). SEM micrographs of BP films grown at 1000 °C, 1100 °C, and 1200 °C on 3C-SiC(100)/Si and 3C-SiC(111)/Si substrates are shown in Figure 5. The BP films grown at 1000 °C and 1100 °C were typically dark red and had highly faceted crystallites with four-fold symmetry representing the BP(200) orientation on 3C-SiC(100)/Si and three-fold symmetry representing the BP(111) orientation on 3C-SiC(111)/Si substrates. When the deposition temperature

was increased to 1200 °C on both 3C-SiC/Si substrates, the films turned dark gray and were composed of a combination of regular and irregular faceted grains, indicating that the films were partially polycrystalline. This decrease in crystalline order of BP at 1200 °C was quite contrary to our previous results, where the crystalline order was best at 1200 °C when deposited on 4H-SiC and AlN/sapphire substrates.[8,10] In comparison, BP films had better crystalline orientation and overall quality on 3C-SiC(100), partly due to better crystalline quality of bare 3C-SiC(100) compared to 3C-SiC(111). BP epitaxy on a limited number of 3C-SiC/4H-SiC substrates was also explored. An SEM micrograph of BP film deposited on 3C-SiC(111)/4H-SiC(0001) at 1200 °C is shown in Figure 6. The BP(111) crystallites were highly faceted and had larger grain size on this substrate compared to 3C-SiC(111)/Si. Furthermore, the morphology of the film, with few pits on the surface, resembled to that of BP grown on 4H-SiC(0001) substrates in our previous work.[10]

Figure 6: BP film grown on 3C-SiC(111)/4H-SiC(0001) at 1200 °C.

As discussed earlier, there will be some preexisting strain in the 3C-SiC layer deposited on a Si substrate due to large lattice and thermal expansion mismatches between 3C-SiC and Si. Consequently, BP films grown below 1200 °C cracked occasionally when deposited on the already strained 3C-SiC/Si substrates. Film cracking was more pronounced when the deposition was increased to 1200 °C. One probable cause for the degradation of crystalline order of BP on 3C-SiC/Si substrates could be the increased strain in 3C-SiC at higher deposition temperatures. As a result, the epitaxial orientation of incoming BP atoms with respect to the substrate was disrupted, resulting in polycrystalline films. Another reason for the degradation of crystalline order on 3C-SiC/Si could be due to the diffusion of Si atoms from Si substrate into the BP film through the pinholes in 3C-SiC (shown in Figure 3) and subsequently disturbing the crystal growth and orientation. This can only be proved by comparing the Si impurities in BP films grown on 3C-SiC/Si and 3C-SiC/4H-SiC substrates via SIMS analysis. The above two arguments are consistent with the results obtained on 3C-SiC(111)/4H-SiC(0001), where film cracking and degradation of crystalline order was not observed even at high deposition temperature (1200 °C). This is perhaps due to the deposition of BP on a relatively less strained 3C-SiC layer grown homoepitaxially on a 4H-SiC(0001) substrate, where the lattice and thermal expansion mismatches are similar for both 3C-SiC and 4H-SiC.

Figure 7: AFM images of BP films deposited on 3C-SiC(100)/Si at 1000°C with $\text{PH}_3/\text{B}_2\text{H}_6$ flow ratios of (a) 100 and (b) 150

The thickness of the BP films was measured by examining the cleaved samples in cross section by SEM. The growth rate was approximately 4-5 $\mu\text{m/hr}$. Surface roughness of a few BP films on 3C-SiC(100)/Si was measured by atomic force microscopy and are shown in Figure 7. The RMS roughness value for a film with a thickness of 3 μm , grown at 1000 °C with PH_3 and B_2H_6 (1% in H_2) flow rates of 40 sccm each, was 55 nm. When the B_2H_6 (1% in H_2) flow rate reduced from 40 sccm to 26.7 sccm, roughness of the film with a similar thickness decreased to 15 nm, due to the decreased deposition rate. In addition, orientation of BP(200) crystallites was improved when the flow rate ratio was increased. RMS roughness of BP film on 3C-SiC(100) (15 nm) was the lowest of all substrates tested, including 4H-SiC (36 nm) and AlN/sapphire (27 nm), at identical deposition conditions.

Figure 8: $\theta/2\theta$ XRD relative peak intensity ratios of BP deposited at various temperatures on 3C-SiC(100)/Si (black) and 3C-SiC(111)/Si (red) substrates.

The crystalline orientation of BP films on Si-base substrates was evaluated using X-ray diffraction $\theta/2\theta$ scans by comparing the peak intensities of preferred BP orientations to other unwanted BP orientations. The relative peak intensity ratios of BP films grown on 3C-SiC(100)/Si and 3C-SiC(100)/Si substrates at three temperatures are shown in Figure 8 indicated by black and red lines, respectively. For BP on 3C-SiC(100) layers, intensity ratios of (200)/(111) and (200)/(220) were

highest at 1000 °C, but those ratios decreased sharply with temperature up to 1200 °C. BP(111) was the preferred orientation on 3C-SiC(111)/Si substrate, and so the intensity ratios of (111)/(200) and (111)/(220) were determined. Peak ratios on the 3C-SiC(111) substrate initially increased in the temperature range of 1000 to 1100 °C, but they gradually decreased to the lowest ratio values at 1200 °C, indicating multiple BP orientations. These results were consistent with SEM findings that films deposited at 1200 °C were polycrystalline. Based on the surface morphology and XRD intensity ratios, optimum growth temperatures on 3C-SiC(100)/Si, 3C-SiC(111)/Si and 3C-SiC(111)/4H-SiC(0001) substrates were determined to be 1000 °C, 1100 °C and 1200 °C, respectively.

Table 1. FWHM and strain in BP films deposited at various conditions on 3C-SiC/Si substrates

Substrate	Growth temp (°C)	PH ₃ /B ₂ H ₆ flow ratio	ω FWHM (arcsec)	ω -2 θ FWHM (arcsec)	Theoretical mismatch (%)	Measured mismatch (%)	Out-of-plane strain (%)
3C-SiC(100)/Si	1000	100	1228	761	4.09	4.09	-0.22
	1000	150	1140	748		4.11	0.34
	1100	100	2788	949		4.12	0.46
3C-SiC(111)/Si	1000	100	4041	1088		3.71	-9.42

HRXRD double-axis rocking curves were measured to estimate the film quality and lattice strain in BP films. The FWHM of ω and ω -2 θ rocking curves and lattice strain with respect to BP(100) and BP(111) at various growth conditions are given in Table 1. Peak widths of ω and ω -2 θ rocking curves decreased when PH₃/B₂H₆ flow ratio increased from 100 to 150 at 1000 °C. However, at 1100 °C with similar PH₃/B₂H₆ flow rates, the peak width and out-of-plane strain values increased significantly. As expected, the FWHM and strain values on the 3C-SiC(111)/Si substrate were significantly higher than 3C-SiC(100)/Si substrate at identical temperatures and reactant flow rates since 3C-SiC(111) films are more strained than 3C-SiC(100) films on a Si substrate. In general, the 3C-SiC epilayer has a large lattice constant mismatch and a higher thermal expansion coefficient than the Si substrate.[14,15] Thus, the 3C-SiC films are under tensile strain after cooling from the growth temperature to room temperature.[24–26] Although Raman and HRXRD results showed tensile strain on 3C-SiC(111)/4H-SiC, BP films usually did not crack due to the very small lattice constant and thermal expansion mismatches between 3C-SiC and 4H-SiC.

4. CONCLUSIONS

BP epitaxial films with good crystalline orientation and morphological features were produced on (100) and (111) planes of 3C-SiC epilayers. Rotational twinning in BP was eliminated by depositing it on a crystal symmetry-matched 3C-SiC. Raman imaging revealed uniform peak shift and peak widths, except at defects on the film surface. Raman peak positions of BP on all types of 3C-SiC layers shifted to the lower side, indicating tensile strain in the films. The XRD pattern showed BP(100) and BP(111) to be major orientations on 3C-SiC(100) and 3C-SiC(111). HRXRD rocking curves indicated more strain in BP deposited on 3C-SiC(111)/Si than 3C-SiC(100)/Si. Due to preexisting strain in the 3C-SiC epilayer, BP films on 3C-SiC(100)/Si and 3C-SiC(111)/Si substrates cracked at high deposition temperatures but stayed intact on 3C-SiC(111)/4H-SiC. These results suggest that either high-quality bulk 3C-SiC or 3C-SiC epilayers on 4H-SiC are the substrates for BP epitaxy, as they will produce better quality films than on silicon-based substrates.

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