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Cubic boron phosphide epitaxy on zirconium diboride

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ABSTRACT

Cubic boron phosphide (BP) is one of the least studied III-V compound semiconductors, in part because it is difficult to prepare in high quality form. In this study, zirconium diboride (ZrB_2) was studied as a potential substrate for BP epitaxial layers, because of its advantages of a low lattice constant mismatch and high thermal stability. Two types of substrates were considered: ZrB_2(0 0 0 1) epitaxial films on 4H-SiC (0 0 0 1) and bulk ZrB_2(0 0 0 1) single crystals. The optimal temperature for epitaxy on these substrates was 1100 °C; higher and lower temperatures resulted in polycrystalline films. The BP film/ZrB_2 interface was abrupt as confirmed by cross-sectional transmission electron microscopy, attesting to the stability of ZrB_2 under BP deposition conditions. The BP films were under compressive and tensile strain on ZrB_2 and ZrB_2/4H-SiC substrates, respectively, as determined by Raman spectroscopy, due to differences in the substrate/film coefficients of thermal expansion. This study suggests that with further optimization, ZrB_2 can be an excellent substrate for BP epitaxial films.

1. Introduction

There are two binary boron-phosphorus compound semiconductors, boron monophosphide (BP) also known as cubic boron phosphide [1–3], and boron subphosphide (denoted as $B_{12}P_2$ or B_6P) also known as icosahedral boron phosphide [1,4]. Both semiconductors are potentially suitable for solid state neutron detectors [5,6], due to the large thermal neutron capture cross-section of the boron-10 isotope (3855 barns) [7]. Here we focus on the epitaxial growth of BP, an indirect bandgap semiconductor ($E_g = 2.0$ eV) [3,8]. Its distinguishing properties include an ability to exhibit both *n*- and *p*-type conductivity [3,9], a high thermal conductivity (up to 665 $W{\cdot}m^{-1}{\cdot}K^{-1}$) [10,11], and a high hardness (34 GPa) [12]. Besides neutron detectors, it is also under consideration as a photocatalyst for hydrogen evolution [13] and spacers for extreme ultraviolet reflective optics [14].

Single crystal thin films are necessary for many BP device applications, and they can be prepared by chemical vapor deposition (CVD). The best single crystal substrate for BP epitaxy is unclear. Silicon has been a common substrate, but it suffers a large lattice constant mismatch (+20%) and results in high silicon concentrations (10^{19} cm^{-3}) in the BP film at deposition temperatures of 1000 °C or higher, presumably due to diffusion and autodoping [9]. Silicon carbide is a better substrate, due to its smaller lattice constant mismatch (−4.0%), and greater thermal stability than silicon. First used by Chu et al. [15] in 1971, there have been several recent studies of BP epitaxy on 6H-SiC, 4H-SiC and 3C-SiC [16–18]. As a substrate, silicon carbide does have the potential disadvantage of autodoping the BP with silicon and/or carbon. Aluminum nitride, in the form of epitaxial layers on sapphire, is also a suitable substrate for BP [19]. Its advantages include an even smaller lattice constant mismatch (−3.0%) than SiC, and a larger coefficient of thermal expansion than BP, which results in compressively stressed films, lowering the tendency for the BP films to crack, which they do under tensile stress when deposited on Si and SiC.

Here we consider zirconium diboride (ZrB_2) as a substrate for BP epitaxy due to its high thermal stability and small lattice constant mismatch with BP (−1.3%). The coefficients of thermal expansion of ZrB_2 and BP are roughly 6×10^{-6} to 7×10^{-6} K^{-1} from 300 K to 1000 K [20] and 3.0×10^{-6} to 5.4×10^{-6} K^{-1} from 300 K to 1000 K [21], respectively. It also shares boron as an element common to both the film and the substrate. It is a refractory material with a hexagonal crystal structure (AlB_2 type structure) formed by layers of boron atoms in honeycombed, graphite-like sheets, stacked between hexagonal close packed layers of zirconium. With a high melting point (3230 °C) [22], ZrB_2 should be stable under all practical deposition temperatures and hence noncontaminating. It has a high electrical conductivity (7.0×10^{-6} $\Omega{\cdot}cm$) [23] due to its metallic bonding and electron transfer from the metal to boron sheet. This is advantageous for vertical devices, as it minimizes the electrical resistance of the substrate. It is available as epitaxial

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layers on Si, SiC, and Al_2O_3 [24–26] and bulk crystals [27–29]. All these properties make it a potentially suitable substrate for growing BP films. Here, ZrB_2(0 0 0 1) buffer layers on 4H-SiC and bulk ZrB_2(0 0 0 1) crystals were tested as substrates for BP epitaxy.

2. Experimental Methods and conditions

The ZrB_2(0 0 0 1) films on 4H-SiC(0 0 0 1) employed in this study were prepared by high temperature direct current magnetron sputtering as developed by Tengdelius et al. [24–26]. Briefly, this consisted of sputtering from a ZrB_2 target onto a 4H-SiC(0 0 0 1) substrate heated to 900 °C. The bulk ZrB_2(0 0 0 1) substrates were diced and polished from a crystal that was grown by a float zone technique by Otani et al. [27].

The BP CVD reactor and sample preparation procedure were previously described by Padavala et al. in a study of BP epitaxy on 3C-SiC [18] and AlN/sapphire [19] substrates. Most BP films were grown on ~400 nm ZrB_2(0 0 0 1) buffer layers deposited on a 407 μm thick 4H-SiC(0 0 0 1) wafer; a few were deposited on ~ 390 μm thick bulk ZrB_2(0 0 0 1). Substrate areas were 0.5 cm^2–1.0 cm^2. The temperature of the substrates was calibrated against the thermocouple readout by melting a silicon substrate on the susceptor under actual reaction conditions. The deposition temperature mentioned throughout this paper, deduced from the thermocouple readout, is expected to closely approximate the surface temperature of the substrates. Substrates were heated to 1200 °C under H_2 flow for 15 min to clean the surface prior to BP deposition. After this *in-situ* H_2 etching, the temperature was reduced and stabilized at the deposition temperature (1000–1200 °C). After achieving a stable temperature, PH_3 was introduced into the carrier gas stream and flowed throughout the deposition process. The deposition time started when B_2H_6 flow was introduced and ends when it was stopped. After the deposition, the temperature is slowly reduced to room temperature. PH_3 was flowed during the cooling period until a substrate temperature of 800 °C to prevent BP decomposition by maintaining a phosphorus vapor pressure. All BP films discussed in this paper were deposited for 30 min. The thicknesses were not measured, but were expected to be between 1 and 3 μm over the temperature range 1000–1200 °C, based on measured thicknesses in our previous studies [17–19]. The H_2 carrier gas flow rate was constant at 4000 sccm in all runs. The PH_3 and B_2H_6 flow rates at 1000–1100 °C were at 40 sccm and 0.2 sccm, respectively. At 1200 °C, the PH_3 and B_2H_6 flow rates were increased to 80 sccm and 0.4 sccm, respectively, based on the best results obtained in our previous studies [17,19]. In the present study, the PH_3 and B_2H_6 flow rates (or ratios) at each temperature were not varied.

The properties of the BP/ZrB_2 films were assessed in several ways. The morphology and grain size of films were imaged by optical microscopy and field emission scanning electron microscopy (FEI Nova NanoSEM 230). The orientation of the BP films, whether they were single or polycrystalline, and if other phases were present, were determined by X-ray diffraction (XRD, Rigaku Miniflex II) with a CuKα_1 (1.54 Å) source. Strain in the films and the crystal quality were also evaluated via Raman spectroscopy using a 0.55 m spectrometer (iHR550, Horiba/Jobin Yvon) coupled to an upright microscope (Olympus BX41) and a 633 nm HeNe laser. Whether the films were exclusively BP or contained $B_{12}P_2$ was determined by Raman spectroscopy and XRD. Transmission electron microscopy (TEM) cross-sectional specimens were prepared by gluing two pieces of the samples face-to-face, polishing from both sides of the specimen down to 60 μm in thickness, and finally Ar^+ ion milling to electron transparency. TEM imaging was carried out by using a FEI Tecnai G2 TF20 UT high-resolution TEM instrument with a field emission gun operated at 200 kV and a point resolution of 1.9 Å.

3. Results and discussion

3.1. Growth and morphology of BP films

SEM micrographs of the BP films deposited on both types of ZrB_2 substrates at 1000–1200 °C are shown in Fig. 1. The growth temperature had a strong effect on the morphology and crystalline orientation of BP. On both types of substrates, at 1000 °C, the films had polycrystalline features such as irregular shaped facets. These films resemble the polycrystalline BP films grown at 1000 °C on AlN [19], 4H-SiC [17] and 3C-SiC [18] substrates in our previous studies. Films deposited at 1100 °C had much better crystalline orientation with triangular BP(1 1 1) features. The average grain size increased from 0.5 μm to 2.5 μm as the temperature was increased from 1000 °C to 1100 °C. There was no evidence of $B_{12}P_2$ formation on either type of substrate at this temperature.

At the highest deposition temperature (1200 °C), the films were a mixture of rough, randomly faceted crystallites, relatively smooth regions, and scattered icosahedrons, the latter suggesting the presence of $B_{12}P_2$. XRD and Raman spectroscopy analysis of these films confirmed $B_{12}P_2$ was formed, as discussed in subsequent paragraphs. The rough regions and $B_{12}P_2$ formation are contrary to the results for BP deposited on AlN [19] and 4H-SiC [17] substrates at 1200 °C under same deposition conditions; there the BP films were highly ordered and free of $B_{12}P_2$. The reason $B_{12}P_2$ forms on ZrB_2 substrates but not on the other substrates at a deposition temperature of 1200 °C is unknown, but this behavior was reproduced.

A low-magnification cross-section TEM of the BP film grown on the 400 nm thick ZrB_2 layer on 4H-SiC substrate at 1100 °C revealed the presence of defects in the BP layer (Fig. 2a). The highest density of defects was closest to the BP/ZrB_2 interface, and decreased toward the free surface. Faceting of the BP film was evident. The BP film on bulk ZrB_2 was similar (Fig. 2b).

Higher resolution TEM images of the BP interface with ZrB_2/4H-SiC and bulk ZrB_2 substrates for films grown at 1100 °C are shown in Fig. 3. BP epitaxy was achieved on both substrates. There were many stacking faults and dislocations in the BP films near the interface. The interface was smoother for the BP film on ZrB_2/4H-SiC substrate compared to the bulk ZrB_2 substrate; still there were plenty of twin boundaries on the {1 1 1} planes, stacking faults, and dislocations in the BP. These twin planes (shown in Fig. 3a) indicate the rotational twinning in BP films. Rotational twinning typically happens when there is a mismatch in crystal symmetry between the epilayer and underlying substrate. In the present case, BP has a zinc blende crystal structure and the underlying ZrB_2 and 4H-SiC substrates have hexagonal crystal structure. The preferred orientation of BP(1 1 1) on ZrB_2(0 0 0 1) has a 3-fold symmetry while the hexagonal ZrB_2(0 0 0 1) has a 6-fold symmetry. Due to this difference in crystal symmetry, the BP(1 1 1) film deposits with two different orientations, rotated by 180° with respect to each other. A deep pit was seen at the interface in Fig. 3a, indicating the ZrB_2 film was not uniformly deposited on 4H-SiC prior to the BP deposition. This may be a consequence of the microstructure of ZrB_2 films on SiC [24]. It is possible that grains boundaries are etched faster by the H_2 introduced prior to the deposition of the BP. In summary, there were BP(1 1 1) twins on ZrB_2 substrates due to the difference in symmetry between BP(1 1 1) and ZrB_2(0 0 0 1).

3.2. Crystalline orientation of BP

The XRD patterns for the BP films grown on ZrB_2/4H-SiC substrates at three temperatures are shown in Fig. 4. The diffraction patterns for 1000 °C and 1100 °C were not significantly different; only BP was detected. At 1200 °C, both $B_{12}P_2$ and BP peaks were