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Mechanism for Improved Quality $B_{12}As_2$ Epitaxial Films on (0001) 4H-SiC Substrates Offcut towards [1-100]

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ABSTRACT

Epitaxial growth of icosahedral boron arsenide ($B_{12}As_2$, abbreviated here as IBA) on 4H-SiC substrates intentionally misoriented from (0001) towards [1-100] is shown to eliminate rotational twinning. Comparisons of IBA on on-axis and off-axis c-plane 4H-SiC by synchrotron white beam x-ray topography (SWBXT) and high resolution transmission electron microscopy (HRTEM) confirm the single crystalline nature and much higher quality of the films on the latter substrates. Furthermore, no intermediate layer between the epilayer and substrate was observed for IBA on off-axis 4H-SiC. It is shown that the vicinal steps formed by hydrogen etching on the off-axis 4H-SiC substrate surface before deposition cause the film to adopt a single orientation, a process that is not seen on substrates with either no misorientation, or those tilted toward the [11-20] direction. This work demonstrates that c-plane 4H-SiC with 7° offcut toward [1-100] is potentially a good substrate choice for the growth of high-quality, untwinned IBA epilayers for future device applications.

INTRODUCTION

IBA is a wide band gap (3.20eV at room temperature [1, 2]) semiconductor with the extraordinary ability to "self-heal" radiation damage. This makes it an attractive choice for devices exposed to radiation which can severely degrade the electrical properties of conventional semiconductors [3-8]. With many exceptional properties such as high hardness and temperature thermoelectric, IBA has a particularly intriguing possible application in beta cells, devices capable of producing electrical energy by coupling a radioactive beta emitter to a semiconductor junction [9, 10]. The properties of IBA are associated with its unique crystal structure and stiff bonding. IBA is based on twelve-boron-atom icosahedra residing at the corners of an α-rhombohedral unit cell and As-As chains lying along the rhombohedral [111] axis. Each boron atom occupies a vertex of an icosahedron, and is bonded to five other B atoms as well as either an As atom or another icosahedron [3, 7, 11].

In the absence of native substrates, foreign substrates with compatible structural parameters are necessary for the growth of IBA epitaxial films. To date, this has been attempted on substrates with higher symmetry than IBA such as on Si and on-axis 4H- and 6H-SiC [7, 9-13]. However, growth of a lower symmetry epilayer on a higher symmetry substrate often produces structural variants (rotational and translational) in the film that are related to each other

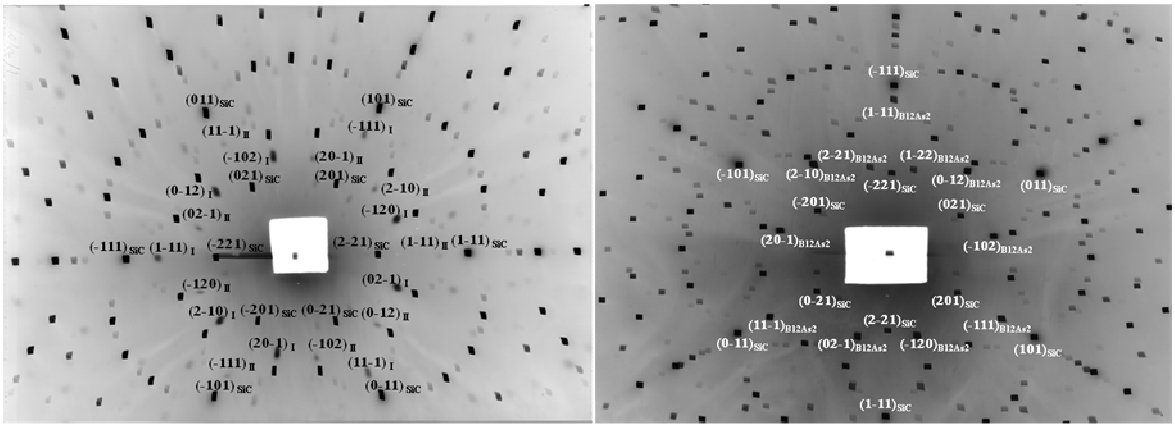
by a symmetry operation that is present in the substrate but absent in the epilayer. A theoretical treatment of this phenomenon, which has been referred to as degenerate epitaxy [14], was carried out by Flynn and Eades [15]. For the case of IBA grown on Si with (100), (110) and (111) orientation and c-plane 6H-SiC, rotational and translational variants are both predicted and observed [7, 11, 13]. Twinning behavior can be diminished by surface roughness or vicinality since the presence of the risers and terraces that comprise the step structures exerts an influence on the nucleation of variants. It has been proposed that m-plane 15R-SiC is potentially a good substrate choice for the growth of untwined IBA epilayers [16]. However, due to the limited resource of pure 15R-SiC substrates, it is very important to discover other good substrates which are commercial-available. Therefore, we have explored the use of commercially available SiC substrates with particular offcut direction to explore this ability to manipulate the relative populations of the multiple variants. C-plane 4H-SiC substrate with 7° offcut toward [1-100] potentially fulfills this requirement. In this paper, growth of IBA on (0001) 4H-SiC substrates with 7° offcut toward [1-100] direction is reported and compared with growth on c-plane on-axis 4H-SiC substrates. It is shown that IBA grown on (0001) 4H-SiC substrates with 7° offcut toward [1-100] is free from structural variants and is of much higher single crystalline quality, in contrast to results from c-plane on-axis 4H-SiC substrate which produced twinned orientations. Factors that contribute to the nucleation mechanism of single crystalline IBA on this specific off-axis substrate are discussed.

EXPERIMENT

IBA was deposited using chemical vapor deposition (CVD) onto hydrogen-etched c-plane 4H-SiC with 7° offcut toward [1-100] direction at 1350°C and 100 Torr of reactor pressure for 2 hours, using 1% B_2H_6 in H_2 and 1% AsH_3 in H_2 as sources. The epitaxial IBA film had a nominal thickness of around 4 μm. The film/substrate orientations were determined by synchrotron white beam x-ray topography (SWBXT). Atomic structure of the interface was examined by high resolution transmission electron microscopy (HRTEM) using a JEOL 2100 system and scanning transmission electron microscopy (STEM) using a Hitachi HD 2700C system at Brookhaven National Laboratory.

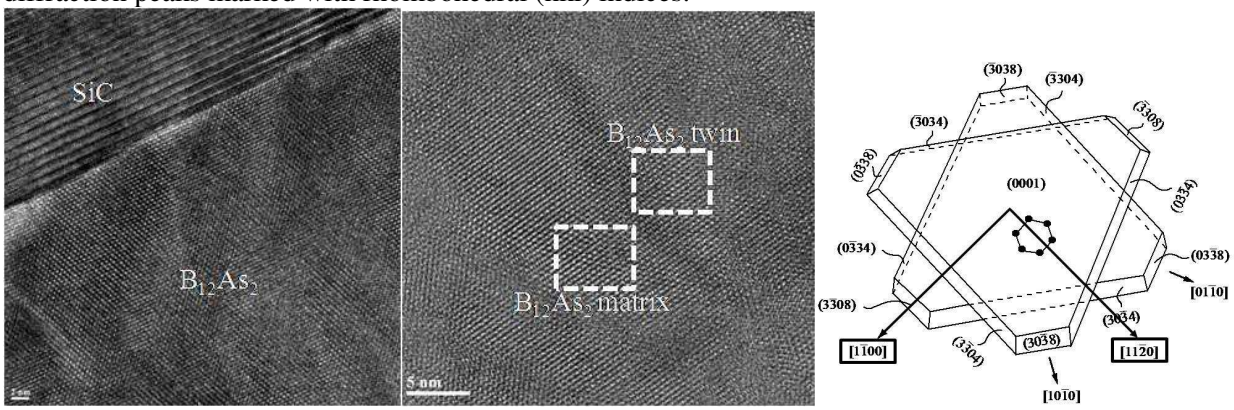
RESULTS AND DISCUSSION

Figure 1 (a)-(b) compares SWBXT Laue patterns recorded from IBA films on both the on-axis and off-axis c-plane 4H-SiC substrates. On the on-axis 4H-SiC, the IBA produced only weak and diffuse diffraction spots that exhibited the type of streaking that is indicative of mosaicity. Indexing of the Laue patterns shows that the IBA has grown in twin related domains, mutually rotated by 180^o about the (111) plane normal. In contrast, on the off-axis substrate, IBA produced much stronger and better-defined diffraction spots. Lower streaking indicated improved mosaicity and decreased strain level. The Laue pattern also lacked any evidence for the existence of twins, indicating the single crystalline nature of the IBA. The absence of twinning and the lower observed mosaicity in films grown on the off-axis 4H-SiC clearly indicates their much higher quality compared to those grown on on-axis 4H-SiC. For the IBA grown on the off-axis 4H-SiC, excellent crystal quality is also apparent in the HRTEM micrograph shown in Figure 2 (a), which shows a strikingly abrupt, clean interface to the substrate. For IBA grown on on-axis 4H-SiC, HRTEM (Figure 2 (b)) confirms the existence of twin related domains.



(a) (b)

Figure 1. (a) Laue pattern of IBA on on-axis c-plane 4H-SiC with subscripts I and II showing diffraction spots from IBA matrix and twin. (b) Laue pattern of single crystalline IBA on off-axis 4H-SiC, with the diffraction peaks marked with rhombohedral (hkl) indices.



(a) (b) (c)

Figure 2. (a) HRTEM image taken along the [10-1] zone axis (equivalent to [11-20] in the hexagonal system) showing a sharp IBA/off-axis 4H-SiC interface and perfect IBA single crystal; (b) HRTEM image taken along [10-1] zone axis showing twin domains in the IBA epilayer grown on on-axis 4H-SiC substrate. (c) Surface morphology of half unit cell height steps in 4H-SiC showing the orientations of the various step risers which have (0001) surface projections parallel to <11-20> (perpendicular to <1-100>).

The significant improvement in microstructural quality achieved when using off-axis versus on-axis (0001) 4H-SiC substrates can be understood by considering the step configurations expected to be exhibited on such substrates with 7° offcut toward [1-100] following hydrogen etching. These step configurations are known to comprise (0001) terraces and two kinds of single bilayer high (quarter-unit-cell-height) step risers; (-3304) which are close-packed and exhibit single dangling bonds and (-3308) which exhibit double dangling bonds. These are shown schematically in Figure 3 (a) (step risers labeled black and grey respectively) which shows that both types of step risers have (0001) surface projections along <11-20> leading to relatively ordered step structures on samples offcut towards [1-100]. This can be contrasted with samples offcut towards [11-20] which will exhibit a much more disordered, zig-zag like step configuration (Figure 2 (c)). Figure 3 shows the evolution of the step structure of the substrate with 7° offcut towards [1-100] during hydrogen etching. The step risers with double dangling bonds will recede at twice the velocity of those with single dangling bond leading to the step bunching depicted in Figure 3(e). This results in the isolation of intersections

between close packed (-3304) step risers and close packed (0001) terraces. When IBA growth is subsequently carried out, IBA molecules that adsorb away from the step risers will generally only be able to weakly bond to the (0001) terraces from where they will most likely desorb. However, the dangling bond configurations exhibited at the isolated intersections between the 1/4c height (-3304) risers and the (0001) terraces enable the IBA molecules to form bonds to both simultaneously and thus nucleate the growth process. This can only happen for one orientation of the IBA thus precluding the possibility of rotational domain formation or twins. Nuclei are expected to spread in both directions from such locations and eventually coalesce.

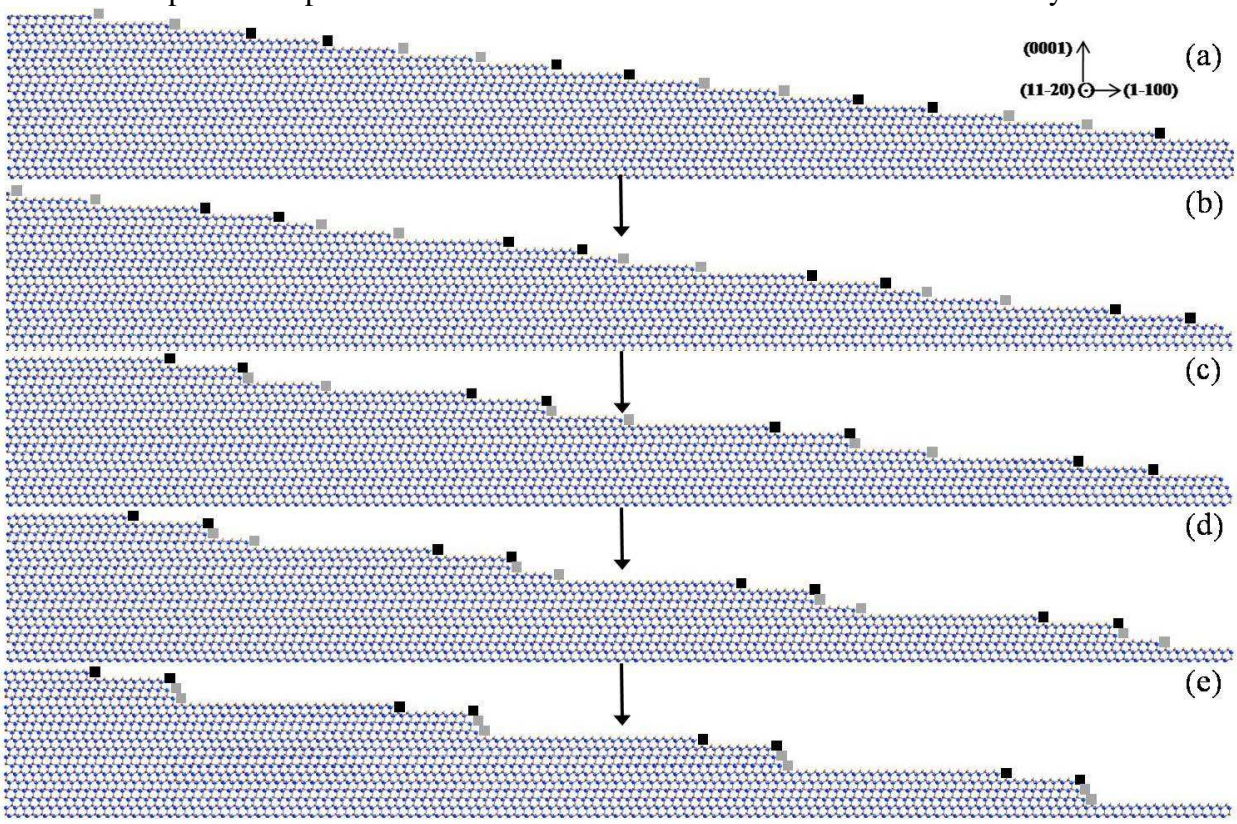


Figure 3. Sequential diagrams showing the evolution of the step configurations created by hydrogen etching of the c-plane 4H-SiC substrate with 7° offcut toward [1-100] direction.

Evidence for the presence of these step structures was obtained using HRTEM and STEM (Figure 4). A series of HRTEM images were recorded along the film/substrate interface and then pieced together (Figure 4(a)). The clean interface and ordered step structures which consist of large step risers with 3/4 unit cell height and small step risers with 1/4 unit cell height are observed. The average terrace width between adjacent risers is around 60nm which corresponds to 3/4c unit cell high step risers and is in good agreement with the step flow theory. Figure 4 (b) shows an STEM image taking from the interface where a 1/4c step riser is observed while in Figure 4 (c), a 3/4 unit cell high step riser is observed. Note that only Si and As atoms can be distinguished under STEM.

The exclusive nucleation of IBA in single orientation at the junction between the 1/4 c high (-3304) step riser and the (0001) terrace is highlighted in the atomic model in Figure 5 (a), enlarged in Figure 5 (b) and from different viewpoints in Figure 5 (c) and (d). Figure 5 (d) shows that the triangular configuration of B atoms at the bottoms of B icosahedra bond to the similarly

oriented triangular configurations of C atoms exposed on the (0001) 4H-SiC terrace. The slight diregistry between domains which expand and coalesce from such nucleation sites can lead to the formation of translational domain boundaries (see Figure 6) while the in-plane mismatch between substrate and the film (~3.7%) can be accommodated by networks of interfacial dislocations.

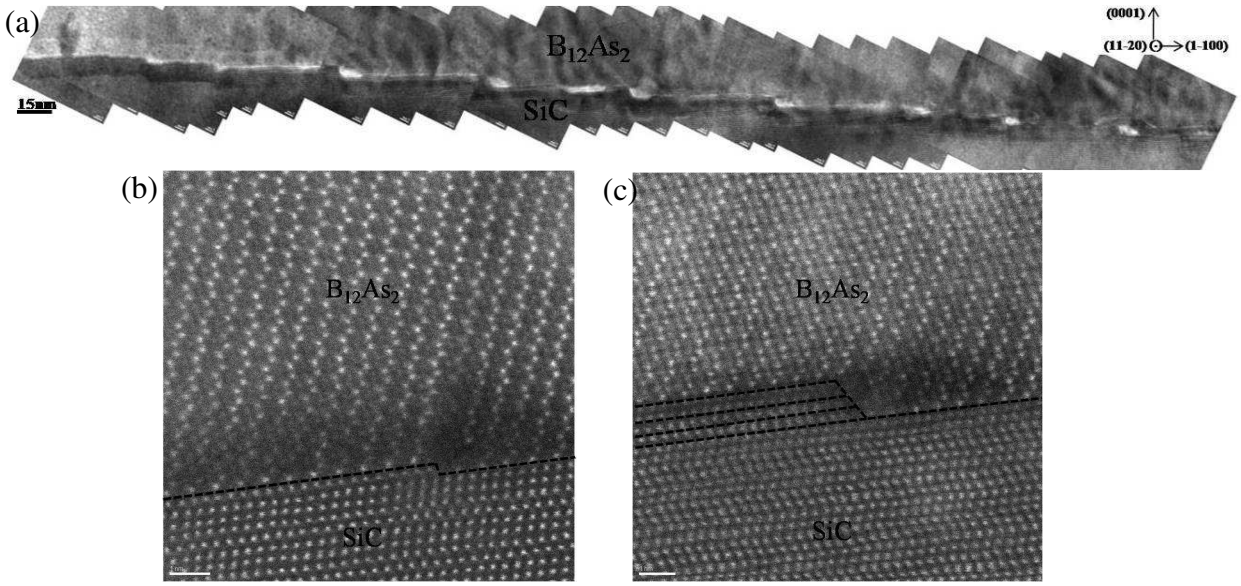


Figure 4. (a) HRTEM images along the IBA/SiC interface showing the step structure of the substrate. (b) STEM image taking from the interface showing 1/4c unit cell height step riser. (c) STEM image taking from the interface showing 3/4c unit cell height step riser.

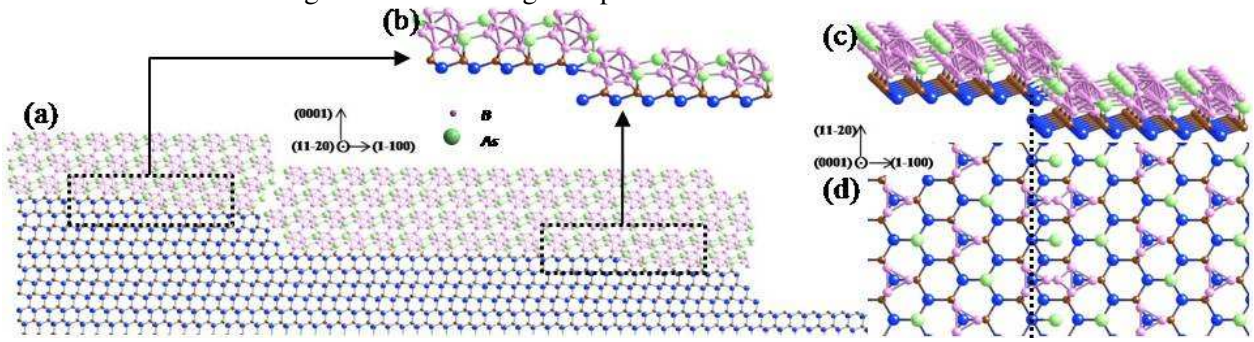


Figure 5. (a) Atomic model of the IBA/SiC interface showing the nucleation sites; (b) magnified image demonstrating the detailed bonding configurations; (c) and (d) perspective view and plan view of IBA nucleated on the surface facets.

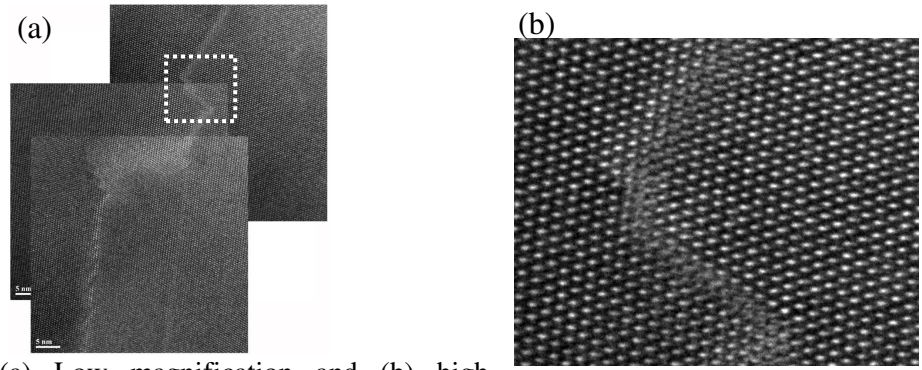


Figure 6. (a) Low magnification and (b) high magnification HRTEM image showing a translational domain boundary in the IBA epilayer.

In conclusion, epitaxial growth of IBA on c-plane (0001) 4H-SiC substrate with 7° offcut toward [1-100] has been discussed. SWBXT, cross-sectional HRTEM and STEM revealed single crystal, untwinned (111) oriented IBA. On the other hand, twin related domains were found in films grown on on-axis 4H-SiC. It is proposed that the single crystalline, untwinned nature of the IBA film resulted from the tendency to nucleate on the isolated junctions between close-packed (-3304) step risers and (0001) terraces present on the hydrogen etched offcut 4H-SiC surface.

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