

Introduction

The chemical vapor deposition and characterization of boron-rich the wide bandgap semiconductors arsenide ($B_{12}As_2$) and boron phosphide ($B_{12}P_2$) was developed. The unusual properties of these semiconductors make them attractive for several applications, including beta cells for the direct conversion of nuclear to electrical energy, thermoelectrics for converting heat to electricity, and neutron detection. Due to their unusual three-atom sharing of two electrons, these boron-rich icosahedral compounds have the ability to self-heal from radiation damage. Consequently, $B_{12}As_2$ is a potentially superior semiconductor for beta cells employing high energy radioisotope beta sources. In contrast, traditional semiconductors are subject to the accumulation of radiation damage and device degradation, unless low energy beta sources are used. With reliable $B_{12}As_2$ beta cells, a much higher energy density than could be provided than by any chemical energy source, lasting for years or even decades.

Because boron is one of the best elements to capture thermal neutrons, devices based on boride semiconductors would also excel in neutron detection. The ^{10}B isotope has one of the largest neutron capture cross-sections of any element, 3840 barns. In contrast, most elements have values of less than 1 barn. Thus, even a relatively thin layer of $B_{12}As_2$ is highly effective at capturing neutrons. In the proposed application, the $B_{12}As_2$ would be both a neutron absorber and detector. A boride semiconductor device would solve the currently unmet critical need for solid state neutron detectors that are compact, fast, and offer high spatial and energy resolution. Such detectors will find applications in neutron scattering, homeland security, and radiation safety. The ability for police and firemen to quickly ascertain whether nuclear radiation is present upon arriving at an emergency situation is a particularly important application of such devices.

Results

Chemical vapor deposition was developed as a means to prepare of thin films of $B_{12}P_2$ and $B_{12}As_2$ for subsequent study. CVD offers good control over the composition of the films as well as controlled doping with impurities. $B_{12}As_2$ heteroepitaxial films (up to 18 μm thick) were deposited on a variety of crystal orientations of 6H-SiC and Si substrates using the hydride reactants, diborane (B_2H_6) and arsine (AsH_3) in a hydrogen carrier. Deposition rates of 2 and 4 $\mu m/h$ were achieved at 1300 $^{\circ}C$ and 1450 $^{\circ}C$, respectively. $B_{12}P_2$ films were deposited from halide reactants, BBr_3 and PBr_3 in a hydrogen carrier exclusively on 6H-SiC substrates.

6H-SiC proved to be the better substrate for $B_{12}As_2$ heteroepitaxy, in terms of the residual impurity concentrations. Films on Si substrates suffered from high concentrations of Si (up to 4 at.%); in contrast, the Si and C concentrations in the $B_{12}As_2$ films deposited on 6H-SiC at 1300 $^{\circ}C$ were at or below the detection limits of secondary ion mass spectrometry (SIMS). The deposition temperature was significant as films deposited at 1450 $^{\circ}C$ contained high residual C and Si concentrations ($>10^{20} cm^{-3}$), probably due to the decomposition of the substrate.

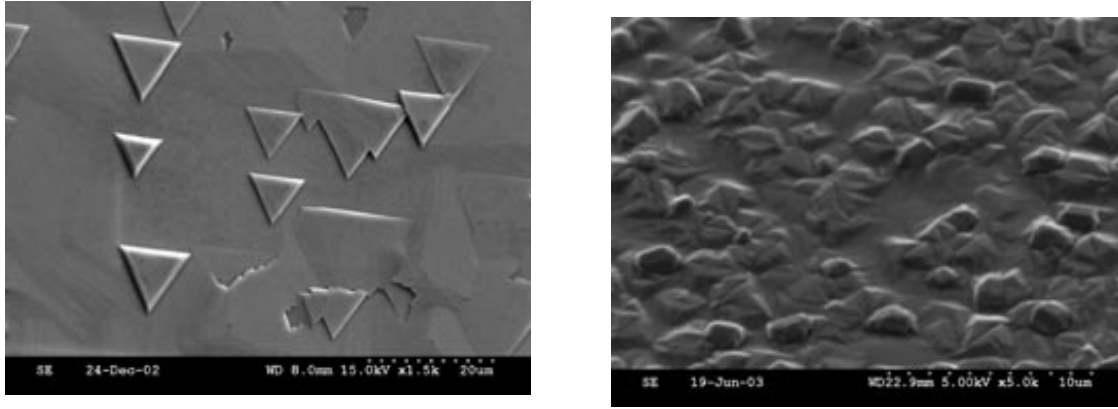


Figure 1 Morphologies of deposited icosahedral borides films deposited on 6H-SiC substrates. (left) $B_{12}As_2$ film deposited at 1550 °C and (right) $B_{12}P_2$ deposited from BBr_3 and PBr_3 at 1700 °C.

The structural properties of the $B_{12}As_2$ films were characterized by x-ray diffraction and transmission electron microscopy. The FWHM of typical high resolution x-ray rocking curves for the (333) peaks of the $B_{12}As_2$ films were 800 arcsec. The films are under tensile strain due to the higher coefficient of thermal expansion for $B_{12}As_2$ than SiC. Rotational twins were present in $B_{12}As_2$ films deposited on (0001) oriented 6H-SiC substrates, as revealed by cross-sectional TEM and x-ray diffraction pole figures.³³ While the c-plane 6H-SiC has six-fold rotational symmetry, rhombohedral $B_{12}As_2$ has only 3-fold symmetry (along its (111) axis), thus it randomly nucleates with two different in-plane orientations.

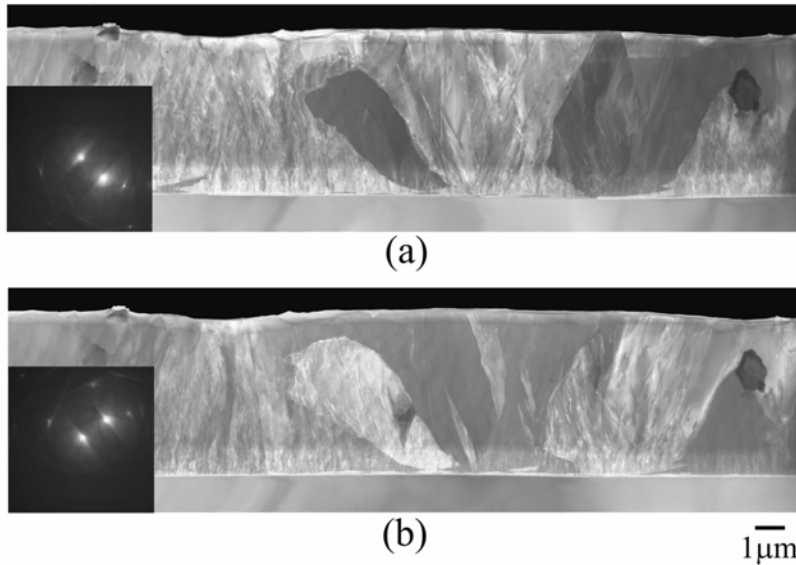


Figure 2 Cross-sectional dark-field electron micrograph of $B_{12}As_2$ on 6H-SiC. In (a), the matrix of the $B_{12}As_2$ epilayer is set at a two-beam condition of $g = 10\bar{1}$; in (b), its included twinned grains are set at a corresponding two-beam condition. Insets show selected area diffraction patterns of the matrix(a) and of the include grains (b).

In addition to rotational twins, a second type of defect was speculated to exist, since the in-plane lattice constant of (0001) 6H-SiC is half that of (0001) $B_{12}As_2$. Because identical lattice sites are available on the (0001) substrates at half the normal distances of the $B_{12}As_2$ lattice, the As atoms and boron icosahedra can be positioned on the substrate with fractional distances of their normal translational vectors. As islands of the $B_{12}As_2$ film merge together, these translational defects may form. These defects are difficult to detect by x-ray diffraction techniques. This type of defect has been seen in other heteroepitaxial system and is described as degenerate epitaxy.

In collaboration with Dr. David Look of Wright Patterson Air Force Base, the electrical properties of $B_{12}As_2$ were measured. The resistivity of *p*-type $B_{12}As_2$ films on semi-insulating 6H-SiC(0001) substrates was controllably varied over nearly four orders of magnitude by changing the concentrations of silicon into the films, incorporated by adding silane during deposition, as shown in Figure 3. The electrical properties of the $B_{12}As_2$ suffered from low hole mobilities, typically less than $3 \text{ cm}^2/\text{V}\cdot\text{s}$. This was possibly a consequence of structural defects in the films. The resistivity of as-deposited undoped and silicon-doped $B_{12}As_2$ films decreased by two or more orders of magnitude after annealing at temperatures above 600°C in argon.

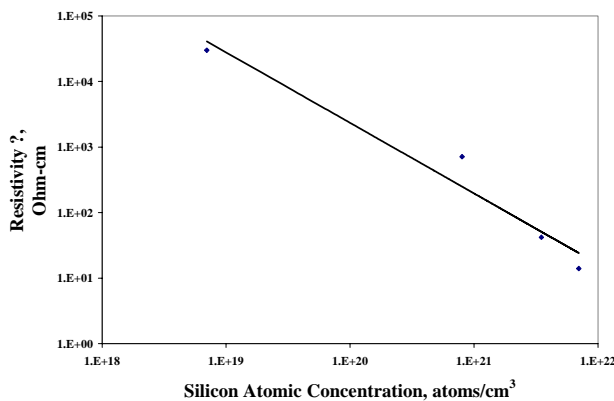


Figure 3 Variation in the room temperature resistivity of $B_{12}As_2$ on semi-insulating (0001) substrates as a function of the silicon concentration as measured by secondary ion mass spectrometry.

The hydrogen concentration in all $B_{12}As_2$ films was relatively high, with a minimum concentration of $3 \times 10^{19} \text{ cm}^{-3}$ in undoped $B_{12}As_2$. SIMS measurements showed that the hydrogen concentration was directly proportional to the Si concentration, reaching values as high as $3 \times 10^{20} \text{ cm}^{-3}$. We speculate that such high hydrogen concentrations may impact $B_{12}As_2$'s electrical properties.

Initial attempts to dope the films n-type by adding selenium were unsuccessful. Despite employing relatively high Se/As ratios, essentially no Se was incorporated into the films, possibly due to selenium's high vapor pressure. However, selenium doping was only attempted at relatively high depositions temperatures, 1450°C and high (>5) As/B reactant ratios, conditions possibly unfavorable for its incorporation.

The properties of palladium, platinum, and chromium/platinum electrical contacts to $B_{12}As_2$ were tested at Penn State. The Pd and Pt contacts exhibited nonlinear I-V characteristics and severe agglomeration upon annealing, but the Cr/Pt contacts were ohmic and remained smooth

even after they were annealed at 750 °C. The specific contact resistance of the Cr/Pt contacts dropped four orders of magnitude after samples were annealed in Ar for 30 s at 750 °C. This reduction in specific contact resistance was linked to a simultaneous drop in the resistivity of $B_{12}As_2$ upon annealing. In subsequent experiments, a low specific contact resistance was also achieved when Cr/Pt was deposited on $B_{12}As_2$ films that were annealed prior to metallization instead of afterwards. This unexpected but reproducible effect of annealing on the resistivity of the semiconductor warrants further investigation.

Publications Resulting From This Research

Investigation of thin film growth of $B_{12}As_2$ by chemical vapor deposition, R. Nagarajan, J.H. Edgar, J. Pomeroy, M. Kuball, and T. Aselage, New Applications for Wide-Bandgap Semiconductors, S.J. Pearton, J. Han, A.G. Baca, J.-I. Chyi, and W.H. Chang eds., (Mater. Res. Soc. Symp. Proc., **764** Pittsburgh, PA 2003) C3.58 on line at:
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Growth of rhombohedral $B_{12}P_2$ thin films on 6H-SiC(0001) by chemical vapor deposition, P. Lu, J.H. Edgar, J. Pomeroy, M. Kuball, H.M. Meyer, and T.L. Aselage, in In Progress in Compound Semiconductor Materials III - Electronic and Optoelectronic Applications, D. Friedman, M.O. Manasreh, I. Buyanova, F.D. Auret, and A. Munkholm eds., (Mater. Res. Soc. Symp. Proc., **799** Pittsburgh, PA 2004) Z2.10.1 on line at:
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Double positioning twinning in $B_{12}As_2$ thin films grown by chemical vapor deposition, W.M. Vetter, R. Nagarajan, J.H. Edgar, and M. Dudley, Mater. Lett. **58** 1331 (2004).

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