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Project Title: **Materials Development for Boron Phosphide Based Neutron Detectors**

Principal Investigator:

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Participating National Laboratory: Lawrence Livermore National Laboratory
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Abstract

The project goal was to improve the quality of boron phosphide (BP) by optimizing its epitaxial growth on single crystal substrates and by producing bulk BP single crystals with low dislocation densities. BP is potentially a good semiconductor for high efficiency solid state neutron detectors by combining neutron capture and charge creation within the same volume. The project strategy was to use newly available single crystal substrates, silicon carbide and aluminum nitride, engineered to produce the best film properties. Substrate variables included the SiC polytype, crystallographic planes, misorientation of the substrate surface (tilt direction and magnitude) from the major crystallographic plane, and surface polarity (Si and C). The best films were (111)BP on silicon-face (0001) 4H-SiC misoriented 4° in the [1-100] direction, and BP on (100) and (111) 3C-SiC/Si; these substrates resulted in films that were free of in-plane twin defects, as determined by x-ray topography. The impact of the deposition temperature was also assessed: increasing the temperature from 1000 °C to 1200 °C produced films that were more ordered and more uniform, and the size of individual grains increased by more than a factor of twenty. The BP films were free of other compounds such as icosahedral boron phosphide ($B_{12}P_2$) over the entire temperature range, as established by Raman spectroscopy. The roughness of the BP films was reduced by increasing the phosphine to diborane ratio from 50 to 200. Bulk crystals were grown by reacting boron dissolved in nickel with phosphorus vapor to precipitate BP. Crystals with dimensions up to 2 mm were produced.

Introduction

Boron compound semiconductors are appealing for solid state neutron detectors due to the high thermal neutron cross-section for the B-10 isotope. Boron phosphide (BP) stands out from other boron compounds because of its ability to be doped both *n*- and *p*-type; many other boron compounds exhibit only one or the other conductivity type. If successful fabricated, devices that convert neutrons to charges and separate the charges in the same volume can be highly efficient, approaching 100% in theory, and hence they can be very sensitive.

The synthesis of high purity-high crystal quality boron phosphide is complicated by its high temperature (~2500 °C) and the high vapor pressure of phosphorus (9,500 MPa) at its melting point.[1] Consequently, epitaxy and flux method growth techniques were employed for this research, as these methods permit the synthesis of BP at relatively low temperatures (<1200 °C). In the case of epitaxy, high purity BP can be produced from the ultrahigh purity diborane (B_2H_6) and boron and phosphine (PH_3).

The most extensive previous studies on BP epitaxy were completed more than 20 years ago, prior to the commercialization of single crystal silicon carbide substrates.[1-3] Most prior studies employed silicon as a substrate, which suffers from a poor thermal stability (diffusion and film/substrate reactions occur above 900 °C) and a huge lattice constant mismatch. Those studies also preceded the extensive development of techniques to optimize compound semiconductor epitaxy on silicon.[4] Epitaxy on silicon was limited to temperatures below 1100 °C. In contrast, silicon carbide is thermally stable to 1400 °C, and its lattice constant mismatch with BP is much lower. Furthermore, aluminum nitride is another potential substrate, that has only recently become available.

Results

Epitaxial BP Growth on Silicon Carbide and Aluminum Nitride Substrates

The quality of BP epitaxial films on eight different types of silicon carbide substrates was investigated and the results from x-ray topography are presented in Table 1.

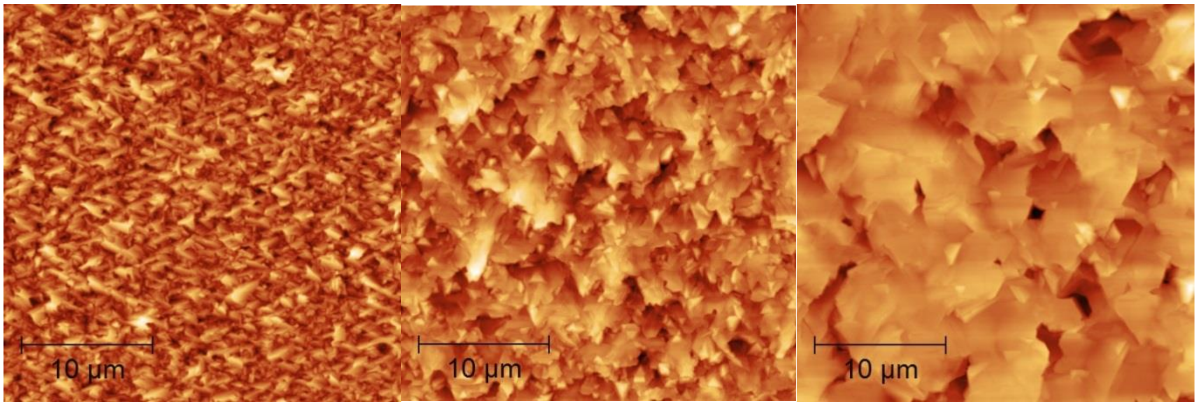
SiC substrate description	**Polarity**	**In-plane twinning?**
4H-SiC, 4° toward [0-110]	Silicon	No
4H-SiC, 4° toward [1-210]	Silicon	Yes
4H-SiC, 4° toward [0-110]	Carbon	Yes
6H-SiC, on-axis	Silicon	Yes
6H-SiC, 3.5° toward [1-210]	Silicon	Yes
6H-SiC, 3.5° toward [1-100]	Silicon	Yes
3C-SiC/Si(100)	Nonpolar	No
3C-SiC/Si(111)	Silicon	No

The problem of twinning arises because of the mismatch of crystals symmetries between the BP which is cubic and has a three-fold symmetry in its close packed plane, ie the (111) plane, and 4H- and 6H-SiC, which has six-fold symmetry. When a BP layer nucleates randomly on a flat hexagonal SiC substrate, it may adopt two distinctly different orientations, in a process known as degenerate epitaxy. In the present investigation, twinning was eliminated by creating a step and terrace surface structure in which all of the steps have exactly the same height and stacking sequence, by using 4H-SiC with its surface plane misoriented the crystallographic (0001) plane specifically by tilting toward the [1-100] direction. *In situ* hydrogen etching of the 4H-SiC substrate with this specific orientation before deposition produces the required step structure. Hence, the BP films on this substrate had the best quality. Twin-free BP films were also achieved on 3C-SiC with both the (100) and (111) orientations, because the symmetry of 3C-SiC matches that of BP.

Boron phosphide (111) films on aluminum nitride films on sapphire (0001) were also successfully prepared. The lattice constant mismatch between BP and AlN is smaller (-3.1%) than for SiC (-4.0). While BP films deposited directly on sapphire peel off, the BP films were stable on AlN/Al_2O_3. Unfortunately, the BP were twinned on these on-axis substrates. Future study on off-axis substrate may eliminate this problem, as was demonstrated for misoriented 4H-SiC(0001). Nevertheless, the BP films on AlN/Al_2O_3 had the highest electron mobility of any of the BP films tested, 240 $cm^2/V\cdot s$. Thus these results for BP on AlN/Al_2O_3 were encouraging, and warrant further investigation.

Impact of process conditions

The impact of the process conditions on the quality of the BP films was also investigated. Depositing at temperatures of 900 °C and lower produced unoriented, polycrystalline films. Increasing the deposition temperature from 1000 °C to 1200 °C increased the ordering and the grain size in the BP layers by more than a factor 20 (Figure 1). Raman spectroscopy and x-ray diffraction confirmed that the films were free of other phases, such as icosahedral boron phosphide, $B_{12}P_2$ at all temperatures. Clearly, depositing at a higher temperature improves the quality of the BP, confirming one hypothesis of the original proposal for this research. Increasing the P/B ratio in the source gases reduced the surface roughness of the films.



(a) (b) (c)

Figure 1. Increasing the deposition increases the BP grain size on 4H-SiC(0001) tilted toward the [1-100] direction, (a) 1000 °c, (b) 1100 °C, and (c) 1200 °C, all deposited for 30 minutes with a PH_3/B_2H_6 ratio of 200.

Flux Growth of Boron Phosphide Crystals

Bulk BP crystals were grown by reacting phosphorus with boron dissolved in nickel. A mixture of 45 atomic % boron and 55 atomic % nickel in a boron nitride boat was placed in one end of an evacuated quartz tube; pure phosphorus was placed at the opposite end. A liquid solution was created by heating the nickel and boron to 1150 °C, then the phosphorus was vaporized by heating to 400 °C. The phosphorus vapor reacts with the dissolved boron to produced BP. Crystals were grown by slowly cooling the solution at 3 °C/hour. Bright red crystals up to 2-3mm in dimension were produced. These crystals had a lower dislocation density than epitaxial films, however, photoluminence spectroscopy suggests the epitaxial films had a higher purity. The main contaminants in the BP crystals will be identified in the near future. Crystals of this type were employed in a study to determine the equation of state for solid BP at high temperature.

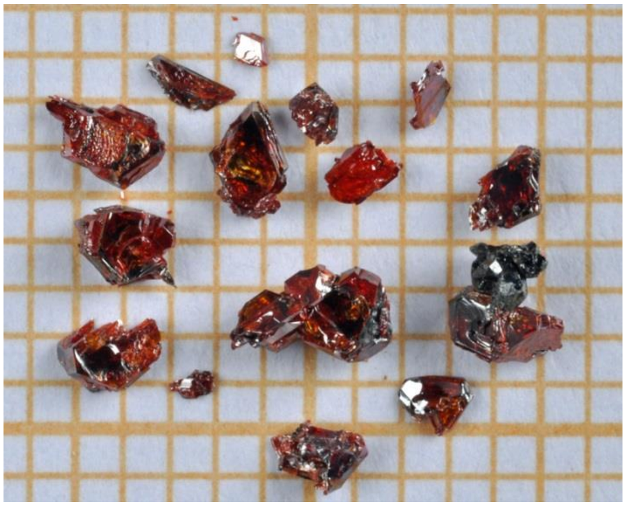


Figure 2 Optical macrograph of BP crystals precipitated from nickel-based. The grid scale is 1 mm.

References

[1] Y. Kumashiro, *Refractory semiconductor of boron phosphide*, J. Mater. Res. **5** 2933 (1990).

[2] K. Shohno, M. Takigawa and T. Nakada, Epitaxial growth of BP compound on Si substrate using the B_2H_6-PH_3-H_2 system, J. Cryst. Growth **24/25** 193 (1974).

[3] T. Nishinaga, H. Ogawa, H. Watanabe, and T. Arizumi, *Vapor growth of boron monophosphide using open and closed tube processes*, J. Cryst. Growth **13** 346 (1971).

[4] D. Zhu, D.J. Wallis, C.J. Humphreys, *Prospects of III-nitride optoelectronics grown on Si*, Rep. Prog. Phys. **76** 106501 (2013).

Papers and/or patents

Single-crystal cubic BP under quasi-hydrostatic pressure, Y. Le Godec, M. Mezouar, O.O. Kurakevych, P. Munsch, U. Nwagwu, JH. Edgar, and V.L. Solozhenko, J. Super Hard Mater. **36** 61-64 (2013).

More papers will be forthcoming.

People Working on This Project

Kansas State University

Principal Investigator J.H. Edgar, department head and university distinguished professor of chemical engineering at Kansas State University received three months of summer support.

Graduate students (three total)
Clint Frye, PhD, was 100% project supported from January 2011 to May 2012, and again was 100% project supported from August 2012 until February 2013. Since then he has been supported by a Lawrence Fellowship, and splits his time between Livermore National Laboratory and K-State. He is expected to graduate in May of 2015.

Ugochukwu Nwagwu was a ChE MS candidate from January 2010 to December 2012. He grew the BP crystals by the flux method. He was 100% on this project from August 2011 to December 2012.

Balabalaji Padavala, ChE PhD candidate, was 100% supported on this project from May 2012 until August 2014. He is expected to graduate in May 2015.

Others
V.L. Solozhenko, Institute for Superhard Materials, Kiev, Ukraine, measurement of BP compressibility at high pressures

Jaime Freitas, Naval Research Laboratory, Washington, DC, photoluminescence spectroscopy

R.J. Nikolic, Lawrence Livermore National Laboratory, CA, performed metal contact deposition and device characterization. She supervised Ugochukwu Nwagwu (summer 2012) and Clint Frye (since February 2013) while they worked at Lawrence Livermore Laboratory.

Research Support for J.H. Edgar
Current
ARI-MA: Collaborative Research: Hexagonal Boron Nitride Based Neutron Detectors, National Science Foundation, 2010-2015, $961, 788 (KSU portion), with J. Geuther (KSU) and Texas Tech University.

Pending
RII Track-1:Two-Dimensional Nanomaterials for Energy and Catalysis Innovation, National Science Foundation, role: co-investigator, $20,000,000, KSU portion direct costs: $2,311,269; JHE's direct cost portion: $301,236 (2015-2020).

Two-Dimensional Crystals and Their Heterostructures, Department of Energy EPSCoR, Office of Science, $4,886,922, role: co-investigator, with nine other faculty in the state of Kansas, 2014-2017.

Bulk Crystal Growth of Hexagonal Boron Nitride, National Science Foundation, $330,984, 2014-2017.

None of the above current or pending proposals overlap with this DOE project.

Cost Status

The original DOE budget for this project was $558,904. This was later reduced and the amount K-State received on this project from the DOE $528,904. Essentially all of these funds were spent.