JOURNAL OF SOLID STATE CHEMISTRY 50, 189–195 (1983)

Freestanding Boron Phosphide Films*

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Received January 26, 1983; in revised form April 25, 1983

Boron monophosphide (BP) exhibits several interesting characteristics that may be applied to a wide range of practical applications. Most recent reported advances of BP technology has been developed using CVD films deposited on a silicon substrate. In this work, a technique to prepare freestanding films of BP is presented. Equipment, data on film deposition rate, and proper growth parameters are discussed.

Introduction

Welker (*1*) first reported interesting semiconductor properties for boron phosphide (BP) in 1952. The crystallographic structure was later reported by Peri *et al.* (*2*). Since that time, only scattered reports of various properties of BP were published until the early 1970's. At this point, interest, primarily in Japan, resulted in extensive growth of CVD BP primarily on Si substrates. The difficulty in preparing usable research samples and single crystals, historically, is probably the main deterrant to the development of any widespread interest in BP as a semiconductor.

Boron phosphide is a covalent III–V compound with the cubic zinc blend structure. It is a semiconductor with potential application in solar energy conversion and as a high temperature semiconductor. In addition, it is extremely hard (*3*) and is very abrasion resistant. BP is practically impervious to most mineral acids and resists corrosion in extreme environments. BP is a semiconductor with an indirect band gap of approximately 2.2 eV. These properties make it a prime candidate for photoelectrochemical applications. BP has high carrier mobility (*4*) for both holes and electrons and is a potential material for use in diodes and transistors. The high thermal conductivity and low thermal expansion of BP make it an excellent choice for microwave and high power rectifier applications. BP has also been suggested as a thermal neutron detection (*5*) material.

Wang *et al.* (*6*) grew millimeter sized crystals of BP from metal (Ni, Fe, Pt, Ge) solution. Chu *et al.* (*7*) reported growth of single crystal films of BP on SiC substrates using CVD techniques with $BBr_3 + PCl_3$ or with $B_2H_6 + PH_3$ as reactant materials. These works have been followed by numerous studies of flux growth (Ni_2P or Cu) (*8*, *9*) and CVD growth (*4*, *10–15*) on Si.

Suzuki *et al.* (*16*) have reported the growth of "free boron monophosphide wafers." This growth procedure deposits a BP film on a silicon substrate and subsequently

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* This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

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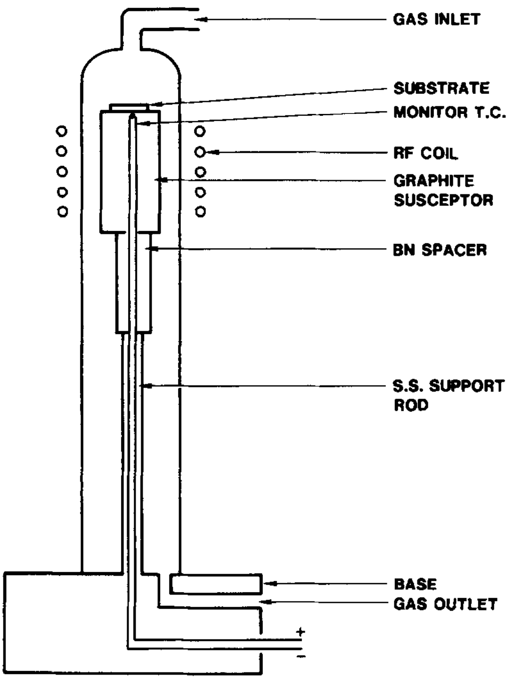

FIG. 1. Physical configuration of growth apparatus.

etches away the silicon leaving the BP as a free film.

In this work, data is presented on the CVD preparation of freestanding films of BP. Deviating from the previously reported required minimum P:B ratio of ≥ 25:1, this study has shown that crystalline BP can be successfully grown with ratios as low as P:B = 0.9:1.

Experimental

The gas nutrient materials used in this work were all Matheson gas products. The hydrogen carrier gas, 99.999% pure, was passed through a Matheson Hydrogen Purifier Model 8363. The diborane, 99.995% pure, was a 1.10% concentration in UHP hydrogen gas. The phosphine, 99.999% pure, was a 4.48% concentration in hydrogen gas. Both the diborane and phosphine were used directly from the gas cylinder.

Matheson gas flow controllers were used to regulate and control all gas flow. The system included Mass Flow Controller, Model 8240, Mass Flow Meter, Model 8142, and Totalizer Model 8122. Each gas system was calibrated for a specific gas mixture. The exhaust gas was passed through a silicone oil gas trap and then either burned or vented through a hood.

The growth apparatus is shown schematically in Fig. 1. The outer atmosphere chamber, constructed of fused silica, was 31 cm in length × 5 cm in diameter and supports the desired growth environment. The chamber is friction fitted into the support base. A gas seal is provided by an "O" ring in the base. This configuration allows the fused silica growth chamber to disconnect from the base, avoiding rupture, should the exhaust tubing become plugged or restricted during a growth procedure.

When operating the growth apparatus shown in Fig. 1, it was noted that the position of the susceptor relative to the rf power coil directly effected successful growth of the BP film. Figures 2 and 3 represent two different susceptor/rf coil relationships. In Fig. 2, the susceptor is high in the rf coil and produces the thermal profile shown to the right. Although the substrate is at the desired growth temperature, the susceptor presents an increasing thermal profile below the substrate. This configuration results in very poor deposition and film growth. In Fig. 3 the susceptor is low in the rf coil resulting in the thermal profile shown to the left. With the substrate located at the high point of the thermal environment, film deposition is successful and freestanding films are produced.

Tungsten, molybdenum, titanium, and tantalum substrate materials were found acceptable for growth of freestanding BP films. The substrates were 2.5 × 2.5 × 0.1 cm in size. Substrate samples were washed in acetone, acid etched, washed in hot absolute methanol, and then loaded onto the graphite susceptor. The atmosphere cham-

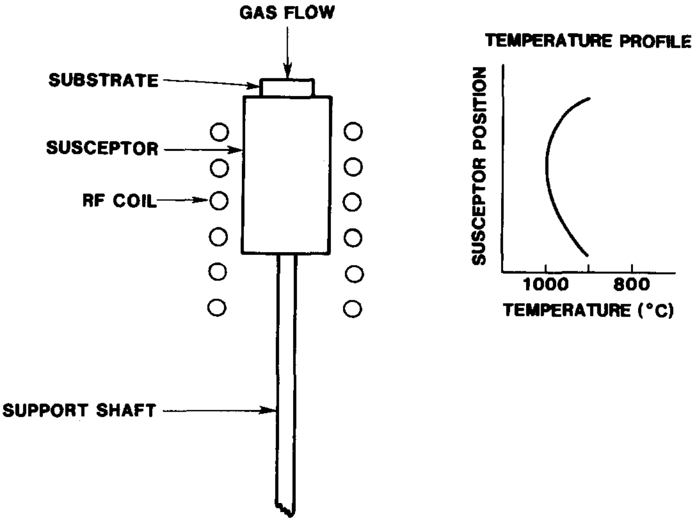

FIG. 2. rf coil/susceptor relationship producing no freestanding BP film deposition.

ber was put in place and the entire system flushed with hydrogen. When the nutrient gas flow rates were established, the hydrogen gas flow rate was adjusted such that the total gas flow rate to the growth chamber was at a constant 2500 SCCM.

Hydrogen carrier gas flow was turned on and power was applied to the rf coil. The substrate sample was heated to 1200°C and thermally etched for a 5-min period. The substrate was then lowered to growth temperature and the nutrient gases were turned on. When growth time had expired, the nutrient gas flow was terminated but the hydrogen carrier gas was continued. The substrate was held at growth temperature for a

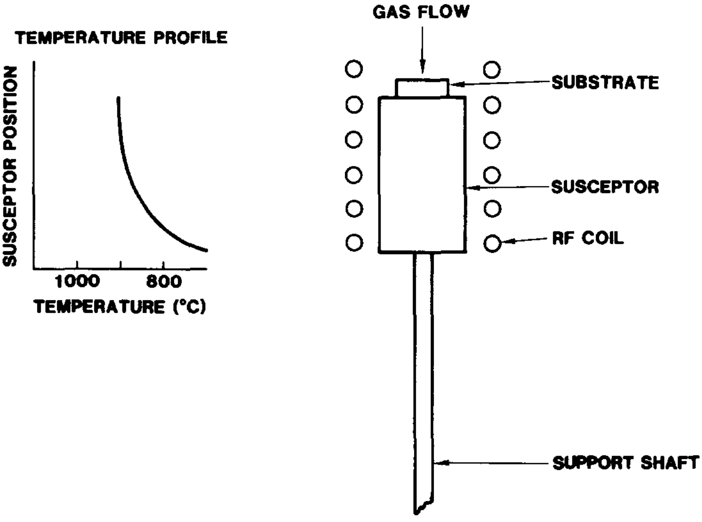

FIG. 3. rf coil/susceptor relationship producing freestanding BP film deposition.

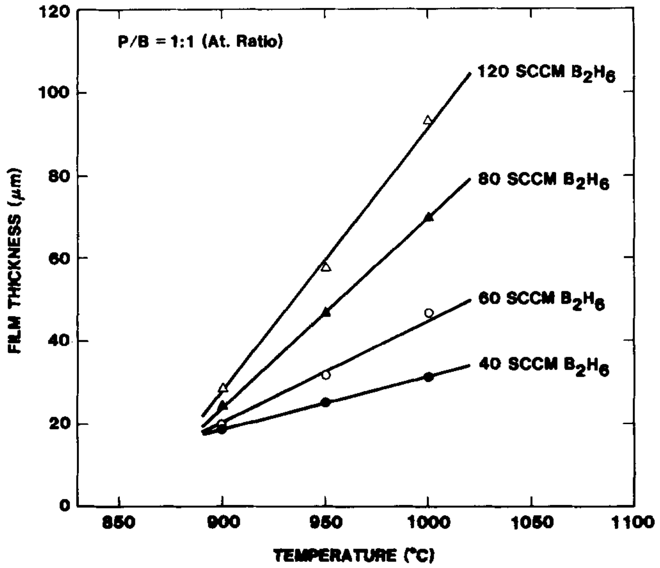

FIG. 4. Temperature dependence of BP film deposition for nutrient gas atom ratio of P : B = 1 : 1 with various nutrient gas flow rates.

5-min soak period. The power was then turned off and the sample allowed to cool. During the rapid cooling period, the BP layer shears free of the substrate and becomes a freestanding film.

Results

Self-supporting, crystalline freestanding films of BP measuring to 25 × 25 × 0.2 mm have been grown. Deposition rates vary

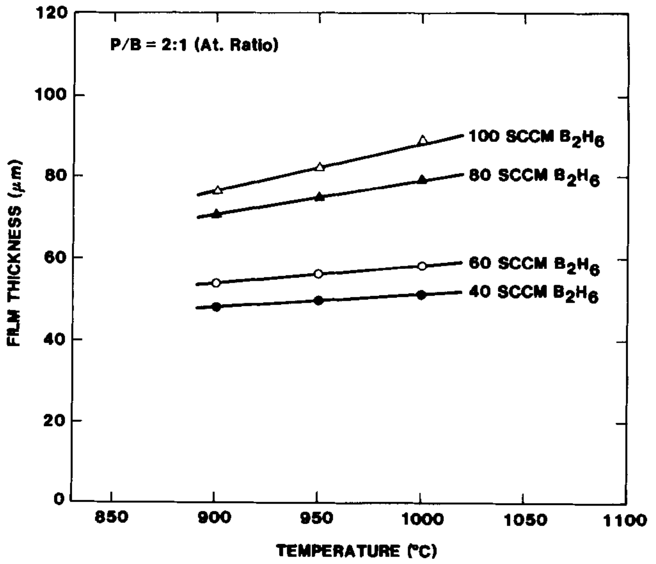

FIG. 5. Temperature dependence of BP film deposition for nutrient gas atom ratio of P : B = 2 : 1 with various nutrient gas flow rates.

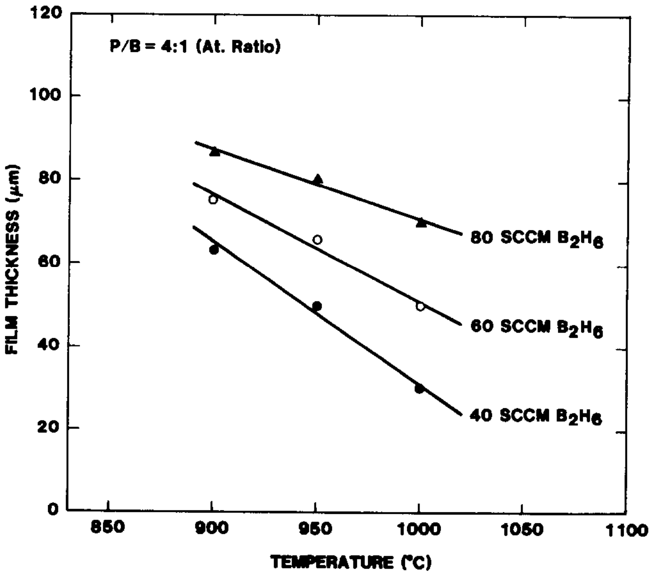

FIG. 6. Temperature dependence of BP film deposition for nutrient gas atom ratios of P : B = 4 : 1 with various nutrient gas flow rates.

slightly for the various substrate materials. The data presented in this study were collected using titanium as the substrate.

Figures 4, 5, and 6 present data on film thickness for growth runs that had a 300-min time duration. Data for growth temperatures of 900, 950, and 1000°C are presented for diborane gas flow rates that vary from 40 to 120 SCCM. Phosphine gas flow rates were adjusted to collect data for gas atom ratios for P : B of 1 : 1, 2 : 1, and 4 : 1.

Figure 4 presents data for a gas atom ratio of P : B = 1 : 1. For this gas ratio film thickness is noticeably increased with higher growth temperatures. The effect of higher temperature on film thickness is greatly increased by increasing the total nutrient gas flow. Increasing the nutrient gas concentrations also significantly increases the film deposition.

Figure 5 presents data for a gas atom ratio of P : B = 2 : 1. At these concentrations, it is noted the temperature has very little effect on deposition rate. The temperature effect is increased with the higher nutrient gas flow. Increased flow of diborane continues to increase total material collected on the substrate.

Figure 6 presents data for a gas atom ratio of P : B = 4 : 1. Increases in total gas flow continues to produce expected increase in deposition. But, at this gas ratio, the higher growth temperatures now produce a striking decrease in film growth rate. It is noted that at this P : B ratio, the effect of increased temperature is decreased with higher nutrient gas flow.

Several general growth characteristics are observed. Increased volume of nutrient gas flow increases film thickness at all temperatures, gas flow rates, and gas atom ratio P : B that were studied in this work. At lower temperature, 900°C, the gas atom ratio P : B exerts a large effect on film deposition. Although BP can be successfully grown with a gas atom ratio P : B = 1 : 1, the large cross sectional area of this physical configuration allows much of the nutrient gases to be carried beyond the hot substrate before reaction is obtained. This nutrient

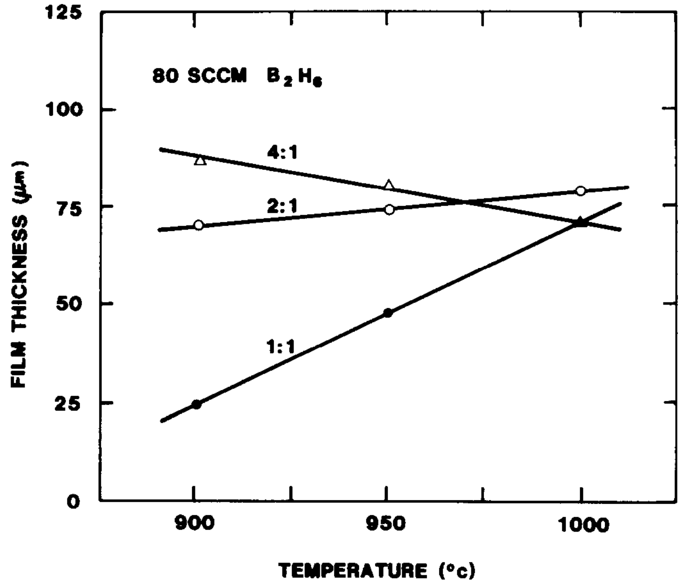

FIG. 7. Temperature dependence of BP film deposition using a diborane gas flow rate of 80 SCCM and various P : B nutrient gas flow ratios.

starvation at the growing interface may be benefited by using larger volumes of phosphine. With a gas ratio of P : B = 4 : 1, the reaction of diborane and phosphine is increased and film thickness is increased.

Although increased diborane gas flow rate does increase film thickness at higher temperatures, 1000°C, the various gas atom ratios P : B (4 : 1, 2 : 1, 1 : 1) have little or no effect on film thickness for any one specific volume of diborane gas flow. Figure 7 presents data for this effect using a diborane gas flow rate of 80 SCCM. Diborane gas flow rates other than 80 SCCM present

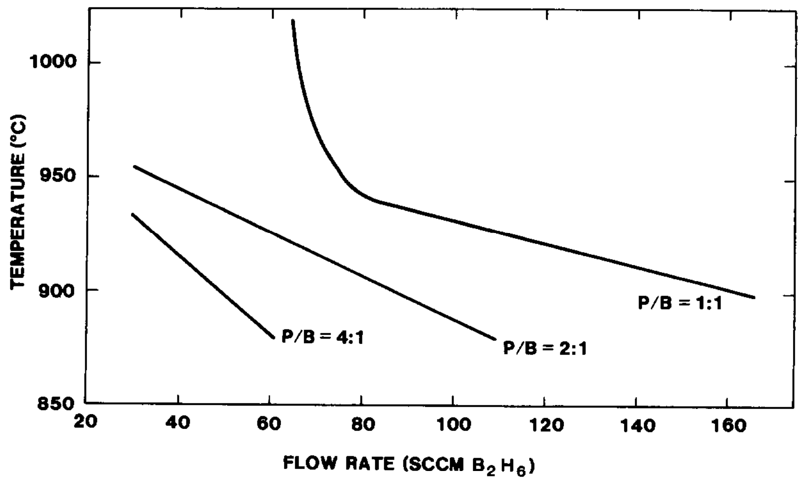

FIG. 8. Deposition field boundaries for producing freestanding BP films.

similar data with line slopes varied for each separate volume. This temperature appears to be more effective in reacting the available nutrient species, even at gas atom ratio P:B = 1:1. As the available diborane gas nutrient is more efficiently utilized, the benefits of oversaturating the atmosphere with phosphine, P:B = 4:1, that was beneficial at 900°C, becomes less important with increasing temperature and eventually disappears at 1000°C.

Although the scope of this study was limited to a narrow range of growth parameter variations, several boundaries that produce freestanding film growth were observed. These data are presented in Fig. 8. In this figure, films deposited using growth temperatures and diborane flow rates that place the growth field above the appropriate P:B ratio boundary line on the chart gave freestanding BP films. Those growth parameters that placed the growth field below the boundary lines produced delicate films that had little or no physical integrity.

X-ray diffraction analysis (PDF 11-119) verifies that the films, at all observed P:B ratios, were single phase crystalline boron monophosphide (BP). Chemical analysis of the freestanding films show no detectable substrate contamination.

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