NASA Contractor Report 181622

Feasibility Studies of the Growth of III-V Compounds of Boron by MOCVD

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Abstract

Boron-arsenic and boron-phosphorus films have been grown on Si sapphire and silicon-on-sapphire (SOS) by pyrolyzing Group III alkyls of boron, i.e. trimethylborane (TMB) and triethylborane (TEB), in the presence of AsH_3 and PH_3 respectively in a H_2 atmosphere. No evidence for reaction between the alkyls and the hydrides on mixing at room temperature was found. However, the films were predominantly amorphous. The film growth rate was found to depend on the concentration of alkyl boron compound and was essentially constant when TEB and AsH_3 were pyrolyzed over the temperature range 550°C to 900°C. The films were found to contain mainly carbon impurities (the amount varying with growth temperature), some oxygen, and were highly stressed and bowed on Si substrates, with some crazing evident in thin (2 μm) B-P and thick (5 μm) B-As films. The carbon level was generally higher in films grown using TEB as the boron source. Films grown from PH_3 and TMB showed a higher carbon content than those grown from AsH_3 and TMB. Based on their B/As and B/P ratios, films with nominal compositions $B_{12-16}As_2$ and $B_{1.1-1.3}P$ were grown using TMB as the boron source.

1. INTRODUCTION

1.1 BACKGROUND

There is limited information available in the literature on the growth of Group III-V semiconductor compounds and alloys containing boron(B) as a Group III element and P and As as Group V elements. Why these materials remain relatively unexplored is not clear, for the III-V boron compounds have potentially attractive properties for high temperature and luminescent devices. BP, particularly, is an interesting semiconductor because it has a high melting point (~3000°C), is stable in composition up to about 1100°C, and is quite chemically inert to normal chemical etchants such as aqueous acids and alkalis. It is also a potential surface passivant for other lower bandgap III-V semiconductors such as GaAs and InP. Its bandgap of 2.0 eV presents a potential advantage over Si for high temperature device use as well as for luminescent applications such as light emitting diodes which operate in the visible, optical switches, facet coatings for lasers, etc. It has been demonstrated that BP can be used as power rectifiers (1), transistors (2), diodes (3) [including tunnel diodes (4)], thermoelectrics (5), coatings for metals (6,7), in single crystal multilayer Si-BP-Si three-dimensional composite structures for future device applications (8); and more recently BP is being studied for use in solid state neutron detectors (9).

Table 1 includes selected properties of the Group III-V boron compounds. Early reports gave the bandgap of BP as 5.9 eV (10,11), rather than the now-accepted 2 eV, and subphosphide and subarsenide composition of B_6V (11,12) rather than $B_{13}V_2$, which appears to be also generally accepted (13,14,19-22). The structure of $B_{13}V_2$ is rhombohedral (14,19), but for convenience, hexagonal dimensions are reported (13).

1.2 PRIOR PREPARATION TECHNIQUES

Several different methods have been reported for the preparation of the B-Group V compounds. These include both closed ampoule and open-tube tech-

Table 1. Selected Properties of Group III-V Boron Compounds

Compound	Structure	Lattice Parameter (Å)	Energy Gap (eV)	Thermal Expan. Coeff.	Refractive Index
BAs	Cubic, Zincblende	a_o = 4.777(15)	1.46(16)		
$B_{13}As_2$	Rhombohedral	a_o = 5.3 α = 70.30°	1.45(20)		
(B_6As)	Hexagonal	a_o = 6.142 c_o = 11.892	1.51(18)		
BP	Cubic, Zincblende	a_o = 4.538(17)	2(18)	$(4.0 \times 10^{-6}$ - $6.2 \times 10^{-6}) K^{-1}$(23) (400-800K)	3.1, 2.3 av.
$B_{13}P_2$	Rhombohedral	a_o = 5.231 α = 69.5°	3.3(19)	$5 \times 10^{-6} K^{-1}$	
B_6P	Hexagonal	a_o = 5.984(13) c_o = 11.850			

niques. Closed ampoule approaches which have been used to produce bulk-type crystals of the B-V compounds include the following:

1. Direct union of the elements at elevated temperatures;
2. Crystallization from metal solvents;
3. Chemical transport; and
4. Reaction of metal phosphide with boron.

Some of the above techniques may also be amenable to open-tube processes.

However, for producing thin layers of the B-V compounds open-tube processes are preferred. Several reactant combinations that have been used to produce boron phosphides are listed in Table 2. Boron arsenide layers have been produced mainly by the pyrolysis of AsH_3 and B_2H_6 mixtures (20,22,24).

A chemical vapor deposition (CVD) method using an open-tube system appears to be the most attractive process for preparing B-Group V compounds, since it lends itself to batch preparation of films. However, the CVD reactions already reported for the preparation of these compounds leave much to be desired. Processes which contain halides or halogens are normally susceptible to impurity problems; unless the quantities of these gases in the substrate region can be precisely controlled, some reaction with the substrate and film during growth can be expected. Some of the autodoping problems reported by Nishinaga et al (26) and Ohsawa et al (27) during the growth of the boron phosphide compounds (e.g. from BCl_3 and PCl_3 in H_2) are undoubtedly due to the reactivity of the substrate with the reactants and/or reaction products as well as reactivity between the hot walls of the reactor and the halide reactants.

The MOCVD process has demonstrated distinct advantages over many other CVD processes for III-V film formation in that it is halide-free, thus minimizing autodoping, is adaptable to conventional epitaxy reactors normally used for elemental semiconductor growth, and requires only one controlled hot temperature zone (the deposition region). Systems for performing large area growth of III-V compounds and alloys are commercially available.

It may be that the autodoping problem that was realized in the B_2H_6-PH_3-H_2 growth process (28) will not occur when a metalorganic is the source of boron and that stoichiometric BP and BAs will be generated at a lower temperature.

This feasibility study is being limited to the use of the hydrides as Group V sources, mainly due to the convenience of working with these high purity gases. The alkyls of As and P are liquids at room temperature and are considered alternate sources worthy of subsequent investigation in combination with the boron alkyls. Since the boron alkyls are poorer electron acceptors than their Al and Ga counterparts, compound formation with AsH_3 and PH_3 (electron donors) is not expected. It remains to be determined if the available B alkyls are either pure enough or the chemistry of pyrolysis and reaction clean enough to generate III-V boron films on Si and sapphire substrates. The results of this feasibility study are reported below.

Table 2. Open Tube Processes Used to Produce Layers of the Boron Phosphides.

Reactants	Reference
$BX_3 + PH_3$ (or $H_2 + P_4$)	11, 35
$BX_3 + PX_3 + H_2$	7, 25, 27, 30-34
$B_2H_6 + PH_3$	8, 9, 19, 21, 28-30, 36-42

To a somewhat smaller extent, n-type or p-type diffused layers are formed in Si substrates during the epitaxial growth of BP on Si when the B_2H_6 - PH_3 - H_2 system is used. Takenaka (28) reports, however, that BP layers do not act as a diffusion source and this is due to small amounts of boron and phosphorus that cover the substrate surface during the early stages. Kim and Shono (29) have also shown that n-BP acts as a n-type diffusion source of phosphorus in Si and p-BP, a p-type diffusion source of boron in Si.

The use of boron hydrides other than B_2H_6 in the preparation of B-Group V compounds may also lead to problems in doping control, since many of the boron hydrides are quite unstable at relatively low temperatures and decompose into polymeric B-H forms which may react with the group V sources such as AsH_3 to produce impure, non-stoichiometric boron-V compounds.

An alternate to the above growth processes which has not been reported for the growth of epitaxial layers of the boron-P and As compounds is the metalorganic approach (MO-CVD), first reported in 1968 (43) by Manasevit for the growth of GaAs on insulators. Subsequently, the formation of other III-V, II-VI, and IV-VI compound semiconductors was reported using various combinations of metalorganics for providing the Group II, III, and IV constituents and hydrides and metalorganics for the Group V and VI elements (44, 45). A historical account appears in the Journal of Crystal Growth (46).

2. EXPERIMENTAL

The alkyl boron precursors used in this study were triethylborane (TEB), which melts at -93°C and has a vapor pressure of 12.5 mm at 0°C, (from Stauffer Chemical) and gaseous trimethylborane (TMB), with a melting point of -160°C and a boiling point of -20°C (from Strem Chemical). They were stored at room temperature. The AsH_3 and PH_3 were 10 percent mixtures in ultra-high purity hydrogen (from Phoenix Research).

The apparatus used in the film studies was only slightly different from earlier descriptions (47,48) in that a glass rotometer calibrated for H_2 was used for both H_2 and H_2-TMB mixtures. The flow differential due to TMB with a constant H_2 flow defines an arbitrary but controlled and operator-changeable concentration of TMB. The hydride and alkyl lines were kept separate with gas mixing occurring only near the top of the vertical quartz reactor. Initial studies tested the reactivity of the boron precursors with the hydrides at room temperature via a quartz reactor with a T at the top to provide separate flows and to confirm that no solid or liquid reaction product was generated either between them or with impurities in the sources on mixing of the gases.

The alkyls were stored in stainless steel cylinders, the TEB cylinder with a bubbler fitting; the TMB was fitted with a regulator. The N_2 overpressure used by the vendor in shipping was removed by purging the TEB with H_2; the N_2 in the TMB tank was removed by submerging a major portion of the tank in liquid N_2 and vacuum pumping off the volatiles. The tank was then warmed to room temperature, and the regulator was set for 20 psi. A needle valve was used to set the differential flow on the glass rotometer. Pd-purified H_2 was used as the carrier gas at a total flow of about 3.2-3.5 LPM into the vertical quartz reactors fitted with a baffle when the T was not present. The substrates were supported on a SiC-coated graphite susceptor that was inductively heated and rotated at about 25 rpm. Temperatures reported are those of a digital readout of an infrared radiation thermometer (emissivity set at 0.82) sighted on the side of the heated susceptor.

Simultaneous depositions were usually made on a number of different polished substrates. These included sapphire [nominally (0001) oriented], either or both (100) Si and (111) Si, and thin films of (100) Si on sapphire (SOS), the latter mainly (a) as a mask on the sapphire substrate to provide a step-height for easy film thickness measurement after mask removal and (b) comparative data with the film grown on the Si substrate(s). GaAs substrates were used in a few experiments designed to grow mixed crystals of (BGa)As and (AlB)As. Si substrates and/or films were given a HF-dip and a thermal etch at 900°C-950°C for at least 10 minutes in H_2 before film growth. When GaAs substrates were present, AsH_3 flow was initiated at about 550°C; and no high temperature etch was used after a HF dip of the companion Si wafers/films.

Due to the fact that the experiments are predominantly feasibility studies analytical data and observations are incorporated in each section dealing with the specific material grown rather than in a remote section, even though much of the analytical data were obtained later in the program.

3. RESULTS AND DISCUSSION

3.1 STUDIES USING TEB

3.1.1 Film Growth Using TEB and AsH_3

Because BAs is reported to be unstable above 920°C (15), all experiments were made at temperatures of about 900° and below. The initial experiments which were made with the T-reactor gave no evidence for interaction at room temperature between the TEB and AsH_3 over a 60 minute period, and pyrolysis of the gas mixtures produced highly adherent, reflective, dark and "smooth" films on the substrates. During growth and for several minutes after TEB flow was discontinued, the gases in a burn box in the exhaust section displayed a green color characteristic of boron-containing gases. Viewing the deposit at high magnification revealed the presence of small circular objects of different sizes, some of which appeared to be coalescing, as shown in Figure 1.

At low flows (25 and 50 ccpm) of H_2 bubbled through the TEB, growth (as observed on the sapphire) using the T reactor was relatively slow; and it took several minutes for the sapphire substrate to darken. Increasing the flows to 100 ccpm caused the sapphire to darken in less than 30 seconds. The T reactor was then replaced by a standard one, and the effect of growth temperature on growth rate and film composition was determined.

A series of boron-arsenide films about 3 μm thick was grown in the temperature range from 900°C to 550°C using the same flow of H_2 through TEB (100 ccpm) and 10 percent AsH_3-in-H_2 (250 ccpm). Growth rates were found to be essentially constant (about 0.05±0.01 μm per minute) over this temperature range.

Doubling the flow through the TEB (to 200 ccpm), doubled the growth rate at 900°C also, confirming the expected growth rate dependence on the concentration of TEB. The film, about 6 μm thick, buckled on the Si substrate

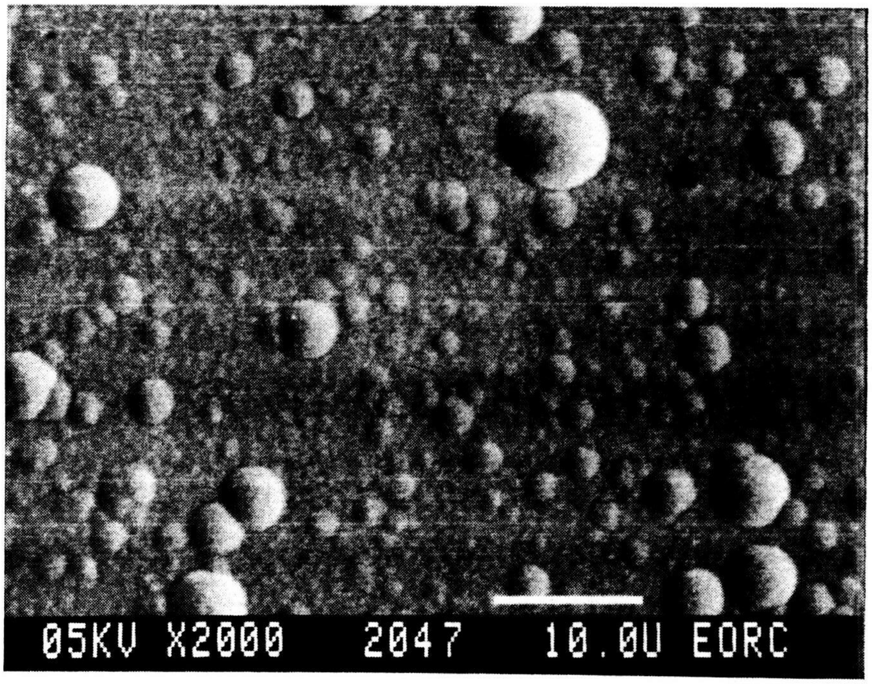

Figure 1. A SEM Photo of the Surface of a Film Grown on Sapphire by Pyrolyzing TEB and AsH_3.

after cooling but failed to buckle on the sapphire and SOS companion substrates, presumably due to smaller thermal expansion differences.

Energy dispersive X-ray analysis (EDAX) revealed As as a major component in the early films (EDAX is not sensitive to B). Subsequent ion-microprobe mass analysis (IMMA) revealed the constituents of several films to be not only rich in B and As but also C, estimated at about 10 percent.

Electron microprobe analysis (EMPA) of the films (Table 3) indicate a steady increase in B content and decrease in As content over the temperature range 550°C to about 675°C, a leveling off in B and As for T = 700-850°C, (pyrolysis of TEB in H_2 and AsH_3 appears to be complete at about 675-700°C), followed by some As loss at about 800°C, and perhaps some B loss at 850°C. The C content changes slowly with temperature, increasing from about 4 percent at 550°C to about 10 percent at 850°C, but increases to over 17 percent at 900°C, perhaps due to more efficient pyrolysis of the volatile organic products of TEB decomposition, such as ethylene (50). Small amounts of O, up to about 0.3 atomic percent, were also measured. The results seem to be consistent with the Auger analysis (AES) profile shown in Figure 2 for sample 39 of Table 3 after removal of about 1500A from the 2.8 µm-thick film.

EMPA of the films grown simultaneously on sapphire yielded compositions which were for the most part the same as that measured on Si.

A transmission measurement of a reddish-brown "boron arsenide" film on sapphire made over the IR range 0.5 to 2.5 µm suggested a bandgap value of about 1.65 eV, only slightly higher than that reported for the boron arsenides listed in Table 1.

3.1.2 Pyrolysis of TEB in H_2

Somewhat similar surface characteristics to those shown in Figure 1 were found for a film grown on sapphire by decomposing TEB in H_2 at 900°C in the absence of AsH_3. A dark film formed on the sapphire, and white deposits coated the cold reactor walls both upstream and downstream of the heated

Table 3. Electron Microprobe Data for Films Grown from TEB and AsH_3 Over the Temperature Range 550-900°C

Sample No.	Substrate	Growth Temp. (°C)	Film Thickness (μm)	Atomic Percent				B/As In Solid
				B	As	C	O	
43	Si(100)	550	3.4	68.4	27.2	4.11	0.26	2.5
	Sapphire		3.5	70.0	26.1	3.89	--	2.7
42	Si(100)	625	3.2	76.4	19.4	4.09	0.19	3.9
	Sapphire		3.2	74.1	21.4	4.24	0.32	3.5
41	Si(100)	703	3.0	79.5	15.0	5.23	0.29	5.3
	Sapphire		3.0	78.2	16.1	5.46	0.26	4.9
40	Si(100)	775	2.5	78.1	15.0	6.83	0.03	5.2
	Sapphire		2.5	78.6	14.4	6.83	0.17	5.5
39	Si(100)	850	2.8	78.8	10.2	10.6	0.30	7.7
	Sapphire		2.8	78.4	8.7	12.5	0.35	9.0
44	Si(100)	900	3.0	76.3	6.5	17.2	--	11.7
	Sapphire		3.2	74.4	4.3	21.3	--	17.3

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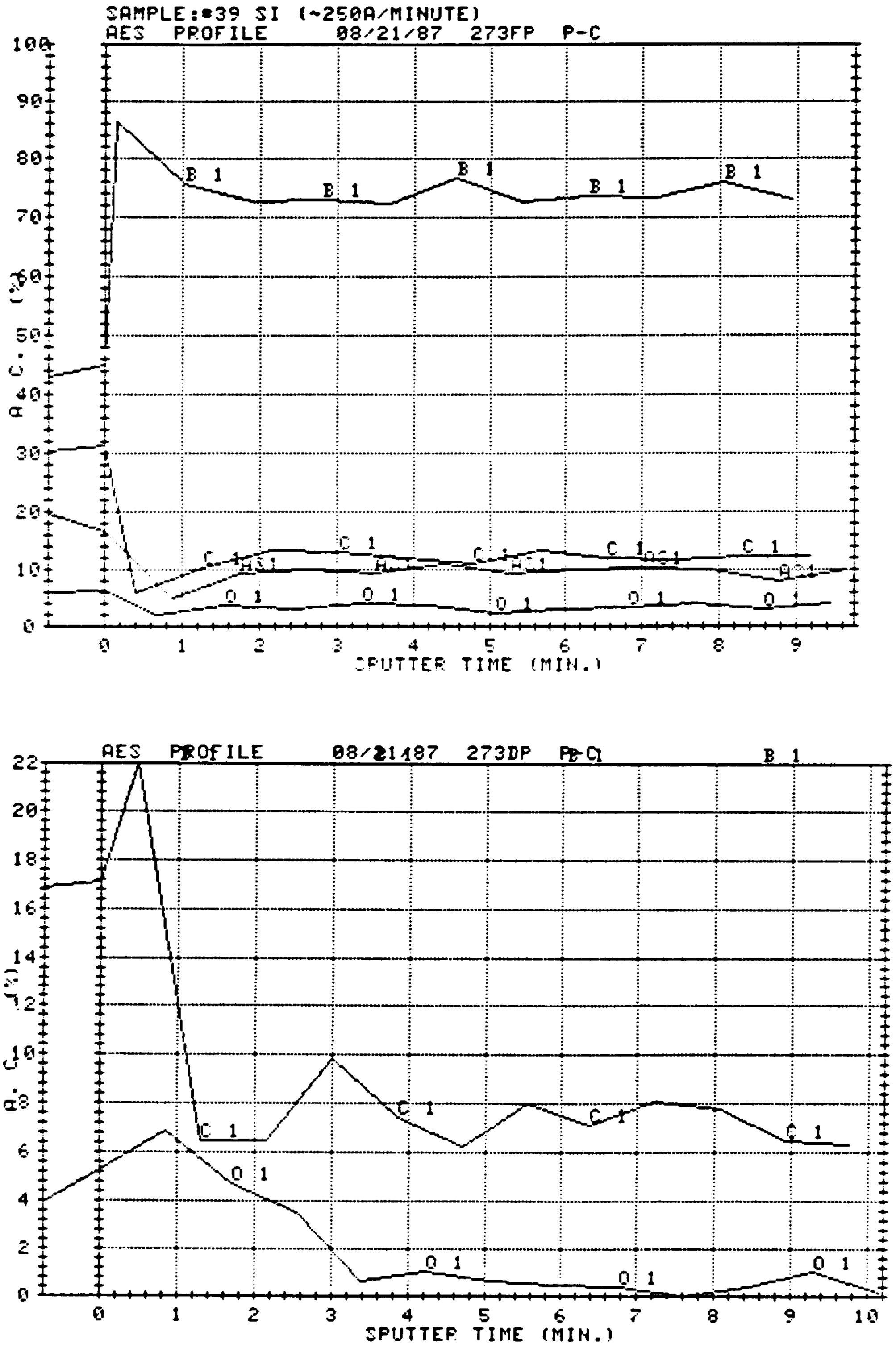


Figure 2. AES Profile of Elemental Analyses of a Boron Arsenide Film on Si Grown at 850°C from TEB and AsH_3.

pedestal. The white deposits appeared to be water soluble and may be alkylhydrides of boron. Studies of the hydrogenolysis of TEB at lower temperatures and high H_2 pressures (49) and of TEB without H_2 (50) have been reported.

IMMA results showed the dark film contained mainly boron and carbon, and a small peak at 27 atomic units was attributed to either Al or BO, probably the latter. If it is BO, then TEB may contain a borate contaminant which may be the source of the oxygen found by AES in analyzed films. IR transmission of the film on sapphire suggested a bandgap of 1.82 eV.

3.1.3 Preparation of Mixed Crystals of (BGa)As and (BAl)As

A few films were grown from mixtures of TEB, trimethylgallium (TMG) and AsH_3, and TEB, trimethylaluminum (TMA), and AsH_3 to generate examples of either mixed crystal films of BGaAs (16) or BAlAs on substrates of Si, GaAs, and sapphire. The films (red-brown in transmission) were grown in the temperature range 750-800°C, with AsH_3 added at about 550°C to stabilize the GaAs substrate. Characteristic peaks attributed to Ga and Al were found in the films via IMMA, but AES indicated the oxygen content in the films was higher than that found in the boron arsenide films (5-9 percent <u>vs</u> 1.5 percent). EMPA showed the films to be surprisingly low in Ga and Al (less than 1 atomic percent). This may be due to reaction of the Ga and Al alkyls with oxygen-containing (borate?) impurities in the TEB. The value of a more-in-depth analysis of the "mixed crystals" is somewhat precluded by the impurity levels in the films.

3.1.4 An Attempt at Multi-layer Growth of GaAs/BAs on Single Crystal Substrates

One experiment was made in the sequential growth of GaAs (a ~4.5 μm thick film grown at 735°C) on a mirrored boron-arsenide film (~0.8 μm thick) grown at 850°C on sapphire and (100)Si (HF-dipped) substrates, with a 10 minute purge between growths. The resulting composites were gray and small grained, with evidence of chipping at the edges of the films grown on the Si. The results indicated a heteroepitaxial composite had not been achieved.

3.1.5 Film Growth Using TEB and PH_3

Studies in this chemical system were similar but not so extensive as in the TEB-AsH_3 studies. T-reactor experiments gave no indication of addition compound formation at room temperature, but film growth studies on Si, SOS, and sapphire substrates in a "standard" reactor produced a black deposit at 1000°C on the side of the pedestal; and the bottom edges of the substrates were also blackened with a crystalline deposit. The films on the top surface, however, appeared smooth and reflective. In this limited study the best appearing films were grown at 950°C. Growth at 710°C led to films that were crazed and crystalline. White deposits were observed on the quartz reactor cold walls for a film growth temperature of 810°C, suggesting intermediate reactions were occurring between the PH_3 and TEB source on heating.

As in the case of the boron-arsenide studies, IMMA revealed the presence of major amounts of B, P, and C in the films grown at 950°C and 1000°C. A band observed at atomic number 47 may be due to P-O. AES of the film grown at 950°C showed as much as 8 atomic percent oxygen in the film, down from the 26 atomic percent measured on the surface prior to removing 200A by sputtering in Ar. The measured B, P, and C levels were respectively 65 percent, 5.8 percent, and about 21 percent.

EMPA of two other films (grown at 810°C and 906°C) indicated the B content was increasing with growth temperature (38 and 45 atomic percent), the P content decreasing (from 46 to 23 percent), and the C increasing (from 15 and 31 percent). The AES and EMPA data show the films are becoming B and C rich. Since the above films were grown using the same H_2 flow through the TEB (100 ccpm) and same PH_3-in-H_2 flow (100 ccpm), it may be that the P concentration at the higher growth tempratures was too low to accommodate the available B species. Studies of growth using higher P/B ratios are suggested.

IR transmissions of several boron phosphide films on sapphire gave values of 2.0 eV, similar to literature values for BP (18) even though carbon contamination was relatively high.

3.2 GROWTH STUDIES USING TMB

3.2.1 Film Growth Using TMB and AsH_3

Using the procedure described earlier for controlling the amount of TMB used for film deposition (Section 2.0), TMB and AsH_3 were initially tested via a T reactor to determine if any reaction occurred on mixing the gases at room temperature. None was evident. Films were grown from TMB and AsH_3 over the limited temperature range of about 840°C to 875°C. The films grown on Si and Al_2O_3 at a rate of about 0.1 µm/min and below were mirror-like, and a 4.3 µm-thick film was not crazed.

Another film, 5.8 µm thick, however, was heavily crazed on Si and slightly crazed on sapphire. At first it was thought the high growth rate of this film (0.38 µm/min) led to poor film growth in an atmosphere low in AsH_3. But subsequent electron microprobe analysis of this and other films grown from TMB and AsH_3 at the lower growth rate indicated the atomic percentages of B (85-87 percent) and As (11-14 percent) in the films were in fact reasonably consistent. Higher B contents and lower C contents (about 2 percent C) were found in films made from TMB and AsH_3 than in films made from TEB and AsH_3 (see Section 3.1.1). The crazing of the 5.8 µm thick film and bowing observed for a 4.1 µm-thick film on Si indicated the film is under considerable stress and that the thermal expansion coefficients of the deposits are considerably different from that of Si.

IR transmission of a 1.6 µm-thick film on sapphire suggested the bandgap to be 1.92 eV, somewhat higher than that reported for boron arsenide films grown from TEB and AsH_3 and for the film produced by pyrolyzing H_2-TEB mixtures (see Section 3.1.2).

If the comparatively low C content in these B-As films made from TMB and AsH_3 is discounted and the B/As ratio is calculated, one obtains film compositions of $B_{6-8}As$ or $B_{12-16}As_2$, not too far out of line with $B_{13}As_2$, a reported subarsenide of B. But the subarsenide is normally produced at growth temperatures greater than 1000°C. Further studies are needed to determine how film composition changes with changes in the TMB/AsH_3 ratio.

3.2.2 Pyrolysis of TMB (without AsH_3)

An experiment in which TMB was pyrolyzed in H_2 at 900°C produced a "metallic-looking" somewhat wrinkled film on Al_2O_3; on Si, however, the film was relatively smooth to the naked eye. An AES profile of the metallic film (see Figure 3) showed it to contain about 85-88 atomic percent B with C and O impurity levels of 6-8 percent and 0-1 percent respectively. EMPA, however, gave values of ~97 percent B and ~3 percent C in the film.

3.2.3 Growth Studies Using TMB and PH_3

It was determined early in the study that the growth of a boron-phosphide film using TMB and PH_3 was quite different from that obtained using TEB and PH_3. As in the case of TEB and PH_3, no reaction between TMB and PH_3 was evident at room temperature, but pyrolysis of TMB and PH_3 mixture at temperatures at and greater than about 900°C resulted in uneven film growth as evidenced by the formation of both reflective and gray crystalline sections on the same substrate. Optical micrographs suggested the gray areas of the "film" to contain spherical balls as shown in Figure 4a; but SEM photos taken at 60° to the surface showed the presence of lightly faceted crystallites of different sizes in hemispherical form (Figures 4b & c). The photos in Figure 4 and 5 support the concept that the crystallites are the result of their formation by pre-nucleation in the gas phase at a finite distance from the substrate surface due to thermal radiation from the hot susceptor.

Cleavage of the substrate and film showed that the crystallites were not imbedded in the substrate but "sitting" on the surface, as shown in Figure 5a

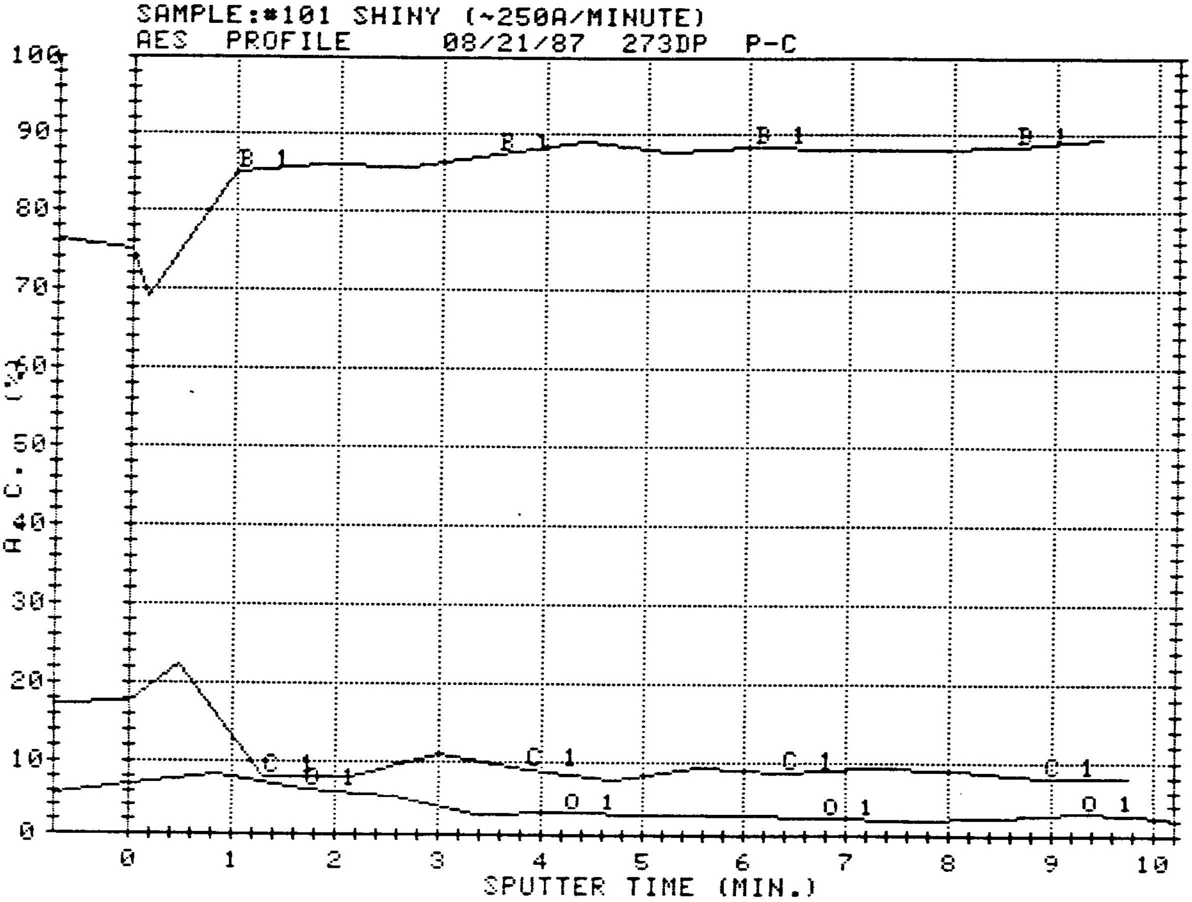
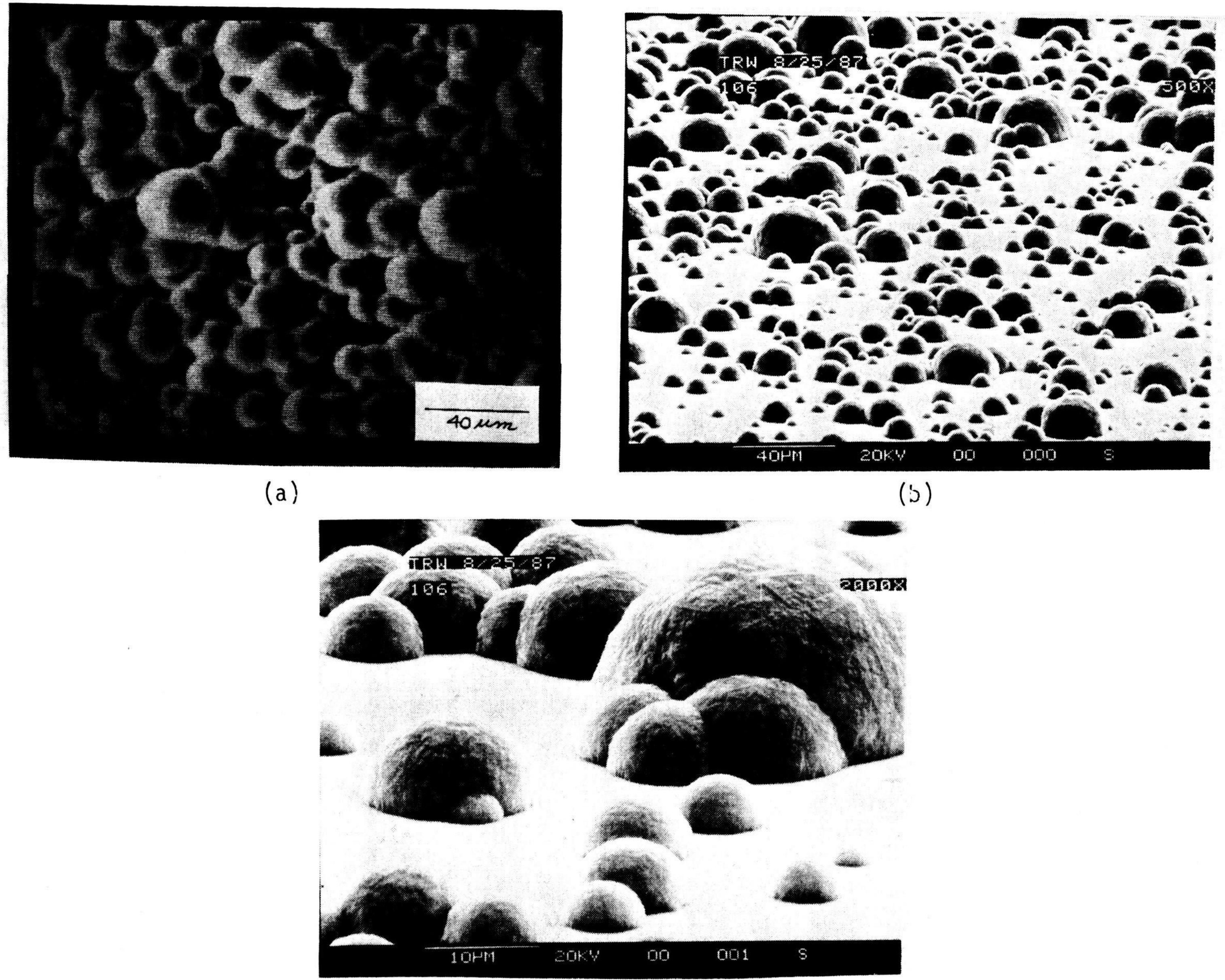


Figure 3. AES Profile Data for B, C, and O in a Film Produced by Pyrolyzing TMB in H_2 at 900°C.



(a)

(b)

(c)

Figure 4. Photos of the Gray Areas of Deposits made on Si Substrates by Pyrolyzing TMB and PH_3 at 900°C: a) taken normal to the surface; b) and c) taken 60° to the surface.

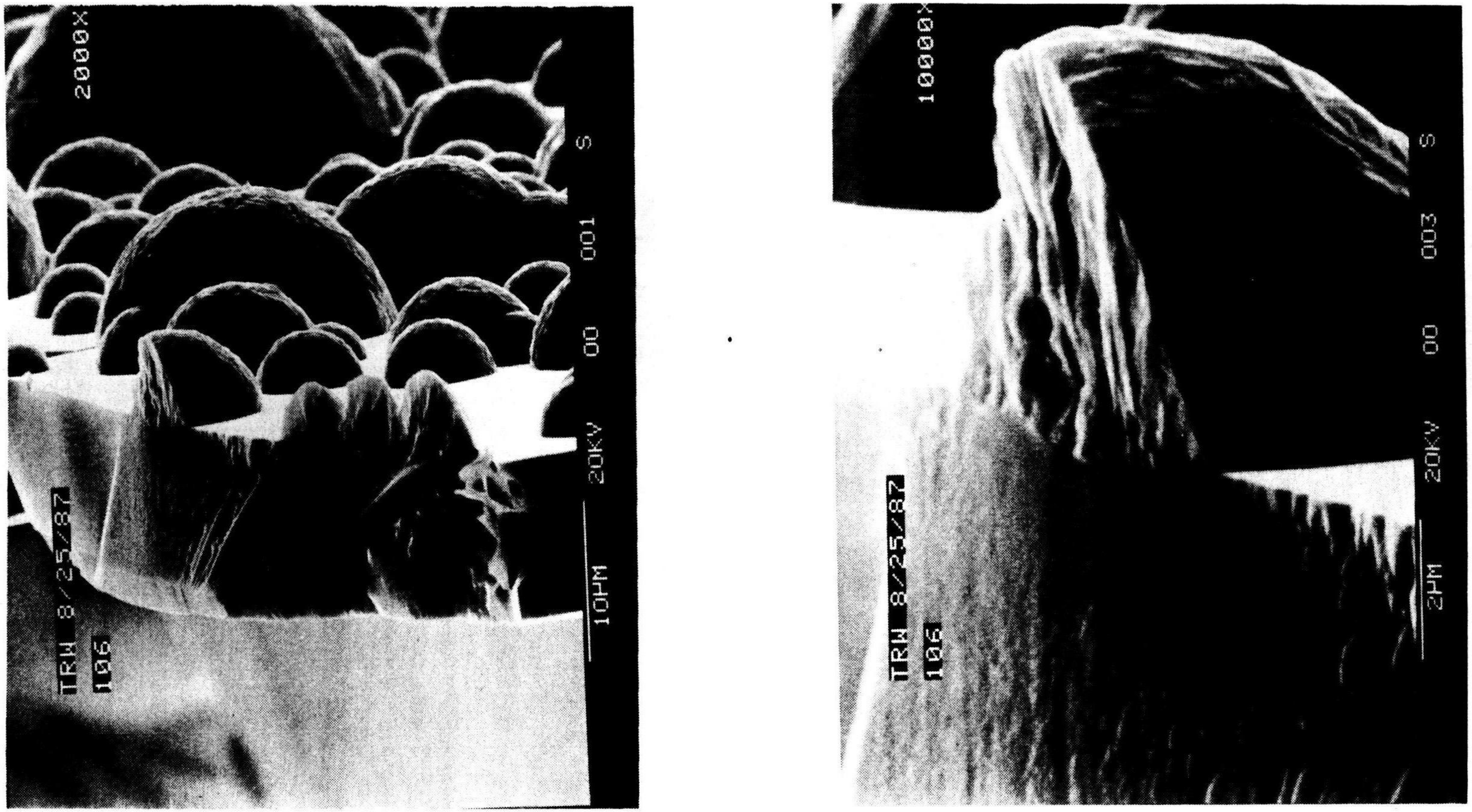
&b, with part of the crystallite in the left center of photo 5a hanging over the edge of the break. Mapping of the crystallites by scanning Auger microprobe/wavelength dispersive X-ray analysis (SAM/WDX) indicated the crystallites contained mainly B, P, and C, which was also found in the flat shiny areas between crystallites and over flat, large areas of the (111) Si substrate. An Auger survey of the reflective area after removal of about 250A from the 8 µm-thick film showed levels of P of about 64 percent; B, about 32 percent; carbon, 3-5 percent; and oxygen, from 0 to 1 percent in the first 2500A of film, values quite different from measurements of a film grown from TEB and PH_3.

By lowering the growth temperature to about 875°C and as low as 850°C, more uniform films essentially free of large crystallites (or nuclei) were produced, but some crazing was evident in films even as thin as 2 µm grown on both (111)Si and (100)Si, similar to that shown in Figure 6 for a 3 µm-thick film. No cracks were seen in the films grown simultaneously on sapphire and SOS. A 9 µm-thick film grown on Si at 860°C flaked off the substrate on being cooled to room temperature with large flakes curving upward, indicating considerable stress in these films as well.

Electron microprobe analyses of several of the thinner boron-phosphide films grown on Si from TMB and PH_3 over the temperature range 850°C to 890°C were somewhat consistent in B (~50 percent), showed a slight increase in P (38 to 46 percent), and showed less C at the highest growth temperature (13 percent at 850°C, 10 percent at 875°C, and about 5 percent at 890°C).

If the C content in the films is not considered and the B/P ratio is calculated, film compositions of $B_{1.1-1.3}P$ are obtained, near that of stoichiometric BP.

The lower carbon content in films grown using TMB as the B source point to its being performed to TEB for both the growth of boron-arsenide and boron-phosphide films. It remains to be determined if the C measured in the films is due to impurities associated with the precursor or inherent in the process of decomposing TEB and TMB in a H_2 atmosphere containing AsH_3 or PH_3.



(a)

(b)

Figure 5. Cleavage of the Deposit of Figure 4 Revealing Under-cutting of the Hemisphere by the Si Substrate (at two different magnifications).

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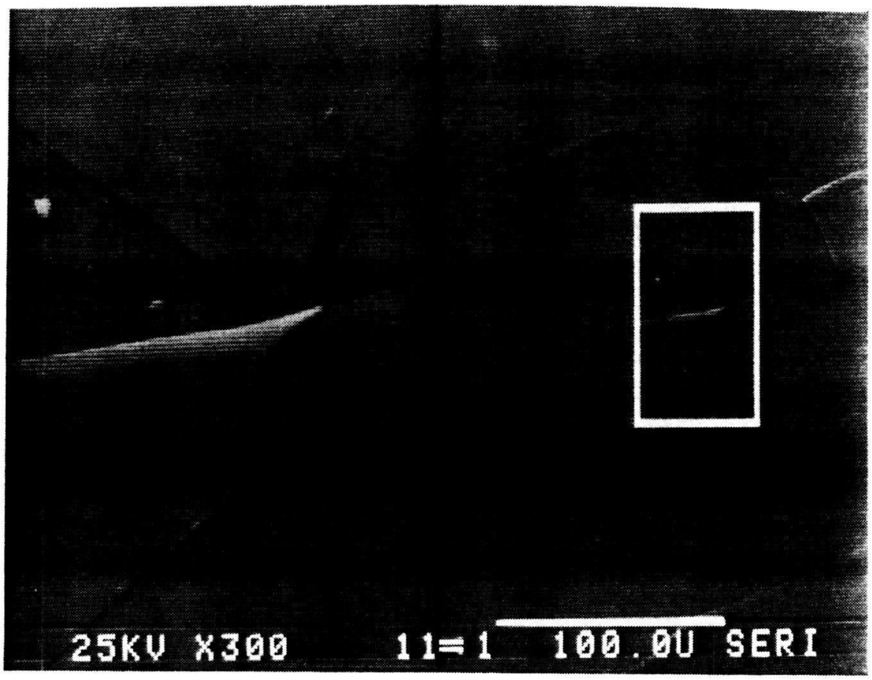

(a) (b)

Figure 6. Crazing Observed in a 3 μm-Thick Film Grown on (111)Si by Pyrolyzing TMB and PH_3 at 850°C: (a) at 300X Magnification; (b) Selected Area

An IR transmission measurement of a 2 µm-thick film of boron phosphide grown on sapphire at 875°C indicated the bandgap to be 2.1 eV, not too different from the film produced from TEB and PH_3, both with relatively high carbon content.

Table 4 contains a summary of compositional and bandgap data measured on several representative films grown during the program.

The presence of relatively high concentrations of carbon (and oxygen) in the films appears to have precluded the growth of single crystals of boron phosphide (BP) and boron arsenide (BAs) even though there were early indications from two different laboratories that at least one of the "BAs"/Si films grown from TEB and TMB and one "BP"/Si film grown from TEB was single crystal (others were reported to be polycrystalline, multiphase, and/or amorphous). The films grown on Si are stressed considerably as evidenced by bowing of the composites and considerable crazing in the films.

Back reflection Laue' patterns taken of composites grown from TEB and AsH_3 early in the program showed only one set of poles (spots on the Laue'). An amorphous film would not be recorded by the Laue', whereas a polycrystalline film would have produced a ring pattern superimposed on the spot pattern due to the substrate. None was evident. A single crystal film on the other hand could have its poles coincident with those of the substrate. Interpretation of the Laue' would not be conclusive.

X-ray diffraction scans at the Unversity of Illinois of these samples, however, suggested to the examiner that the films were, in fact, single crystal. But subsequent chemical analysis revealed that the films grown from TEB were high in C and O at impurity levels that should have precluded single crystal growth. Additional evaluation of these films and data indicated the first conclusion was in error (the 2θ peaks were due to the substrate rather than the film) and that the film is probably amorphous.

Even though C and O were present as impurities, the bandgaps of the films measured, as determined by IR transmission measurements, fell in the range

Table 4. A Summary of Compositional and Eg Data

Process (in H_2)	Growth Temp (°C)	Approx. Atomic Percentage B	C	As	P	O	Eg (eV)	Method of Chemical Analysis
TEB + AsH_3	850-900	75	9	15	--	1.5	1.65	AP
TEB	900			--	--		1.82	IMMA
TEB + PH_3	950	65	21	--	6	8	2.0	AP
TMB + AsH_3	860-900	80-85	2-3	12-13	--	--	1.92	AP
	850-875	85-86	2-3	11-13	--	--	--	EM
TMB	900	85-88	6-8	--	--	0-1	N.M.	EM
		80-85	12	--	--	3	N.M	AP
TMB + PH_3	900	32	3-5	--	64	0-1	2.1	AP
	890	49	5.0	--	46	N.M.	N.M.	EM
	850	49	13	--	38	N.M.	N.M.	EM

NM = not measured
EM = electron microprobe
AP = Auger profile

1.65 to 1.92 eV for the boron arsenides and 2.0 and 2.1 eV for the boron phosphides, the latter being the literature values for BP. Because of their large bandgaps, one might consider using such films for such applications as facet coatings for lasers, for generating amorphous material for solar cells, and/or as high temperature coatings for a multitude of different materials.

The films grown were extremely difficult to remove from any of the heated parts of the reactor system, i.e. the reactor walls, pedestal, and pedestal holder. They are quite chemically inert, particularly in the case of the boron phosphides, as reported by others growing such films (20). Prolonged etching in hot HNO_3 and/or HF-HNO_3 mixtures will remove/undercut a boron-arsenide film attached to the parts made of quartz. Scrubbing with a stiff brush between etching steps will help loosen parts of the film. But prolonged exposure of the HF-containing mixture will etch the quartz, cloud the surface, and require frequent replacement of the etched section.

The boron-phosphides are even more difficult to remove, particularly from the pedestal used to support the substrates. Prolonged exposure to molten NaOH or HF/HNO_3 mixtures was needed to etch/undercut the films on the quartz.

Subsequently, it was necessary to dedicate specific pedestals to either the arsenide or phosphide studies and not attempt film removal between deposition runs since the deposits appeared to be stable in the H_2 environment at high temperatures.

4. CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated that films containing boron and phosphorus and boron and arsenic can be made by pyrolyzing in a H_2 atmosphere Group III alkyls of boron, namely trimethylborane and triethylborane, in the presence of PH_3 and AsH_3 respectively. However, pure and stoichiometric single crystal films of BP and BAs on silicon and sapphire substrates have not been isolated. The films were found to be predominantly amorphous and highly stressed and bowed on Si substrates but much less so on sapphire and silicon-on-sapphire substrates. They contained relatively large amounts of carbon and lesser amounts of oxygen, as determined by Auger and/or electron microprobe analyses. These identified impurities may have precluded the formation of stoichiometric BP and BAs layers. It is not known if the carbon is an inherent byproduct of the pyrolysis of the alkyl boron compound and will always be present in films grown at temperatures up to about 1000°C, or if the carbon is the result of pyrolysis of impurities associated with the alkyl borons.

The C level was lower in films grown using TMB as the boron source and was growth temperature dependent. Films grown from PH_3 and TMB showed a higher C content than those grown from AsH_3 and TMB. Based on their B/As and B/P ratios, films with nominal compositions $B_{12-16}As_2$ and $B_{1.1-1.3}P$ were grown using TMB as the boron source.

Subsequent studies should explore next (a) the use of higher gas phase Group V/Group III ratios as a means for minimizing C contamination; (b) the use of precursors determined to be of high purity; (c) the chemistry of the reactions; and (d) other alkyl sources of boron and Group V elements for producing these high temperature semiconductors.

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The films were grown by H. Manasevit.

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16. Abstract
Boron arsenic and boron-phosphorus films ahve been grown on Si, sapphire and silicon-on-sapphire (SOS) by pyrolyzing Group III alkyls of boron, i.e. trimethylborane (TMB) and triethylborane (TEB), in the presence of AsH_3 and PH_3 respectively in a H_2 atmosphere. No evidence for reaction between the alkyls and the hydrides on mixing at room temperature was found. However, the films were predominantly amorphous. The films growth rate was found to depend on the concentration of alkyl boron compound and was essentially constant when TEB and AsH_3 were pyrolyzed over the temperature range 550°C to 900°C. The films were found to contain mainly carbon impurities (the amount varying with growth temperature), some oxygen, and were highly stressed and bowed on Si substrates, with some crazing evident in thin (2 μm) B-P and thick (5 μm) B-As films. The carbon level was generally higher in films grown using TEB as the boron source. Films grown from PH_3 and TMB showed a higher carbon content than those grown from AsH_3 and TMB. Based on their B/As and B/P ratios, films with nominal compositions $B_{12-16}As_2$ and $B_{1.1-1.3}P$ were grown using TMB as the boron source.

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