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Pyrolysis and film growth studies of phosphinoborane compounds

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Abstract

Chemical vapor deposition experiments were conducted using phosphinoborane compounds of the type $[R_2BPR'_2]_n$, where $R = CH_2CH_3$ (1) or CH_3 (2), $R' = C(CH_3)_3$, and $R = CH_2CH_3$ (3) or CH_3 (4), $R' = Si(CH_3)_3$. Thin films were deposited on Si substrates at 300–850°C under vacuum using 1–3, while no film formed using 4. All films contained considerable carbon (C/B = 0.67–7) and were deficient in phosphorus (P/B = 0–0.5) according to Auger electron spectroscopy. For 3, silicon was incorporated in the films (Si/B = 0.9–2). The preferential loss of phosphorus was nearly complete at higher pyrolysis temperatures that favor formation of carbon-rich films. Volatile products of the decompositions were observed by *in situ* mass spectroscopy and by ^1H nuclear magnetic resonance analysis of the condensate in a liquid nitrogen cooled trap. The products indicate that β-hydrogen elimination of alkene from boron is a preferred reaction pathway, while concerted elimination reactions appear to be inefficient. Although these phosphinoborane compounds do not appear to be suitable precursors for pure boron phosphide, the B-P-C films obtained are chemically inert and may be of interest as protective coatings.

Key words: Boron; Chemical vapour deposition; Thin films

1. Introduction

Boron phosphide (BP) is a material with potential applications as a wide band gap semiconductor [1] and as a hard coating [2]. It is chemically inert and extremely hard, has a high thermal conductivity, and has been synthesized as a *p*-type and *n*-type semiconductor. Crystals of BP can be grown from fluxes at about 1300°C [1,3], while films of BP can be grown by chemical vapor deposition (CVD) at about 950°C from B_2H_6 and PH_3 in H_2 [1,4]. This high deposition temperature limits the applicability of BP films.

The development of single-source precursors, where all of the elements required for the solid state material are contained in the compound, is a promising approach for producing stoichiometric ceramics and semiconductors at relatively low temperatures [5]. One of us has recently reported the synthesis and characterization of several new phosphinoborane compounds, 1–4 below [6]. In the present work CVD experiments using compounds 1–4 were conducted to

$$[R_2BPR'_2]_n \quad \begin{array}{llll} \mathbf{1} & R = CH_2CH_3, & R' = C(CH_3)_3, & n = 1 \\ \mathbf{2} & R = CH_3, & R' = C(CH_3)_3, & n = 2 \\ \mathbf{3} & R = CH_2CH_3, & R' = Si(CH_3)_3, & n = 2 \\ \mathbf{4} & R = CH_3, & R' = Si(CH_3)_3, & n = 2 \end{array}$$

evaluate their potential as single-source precursors to boron phosphide films.

2. Experimental section

Compounds 1–4 were prepared as described previously [6]. Figure 1 shows a schematic of the horizontal low-pressure cold-wall quartz CVD reactor. Si(100) substrates were placed on a graphite susceptor (Poco Graphite DFP-1) that was heated by an IR lamp (Research Inc. Model 5305-05) or an RF induction coil (Lepel Corporation Model T-2.5-1-KC1-BW(T)). Temperature was controlled by a Micristar Digital Controller (Research Inc. Model 828D). The reactor pressure was reduced to 10^{-4} torr prior to the start of the

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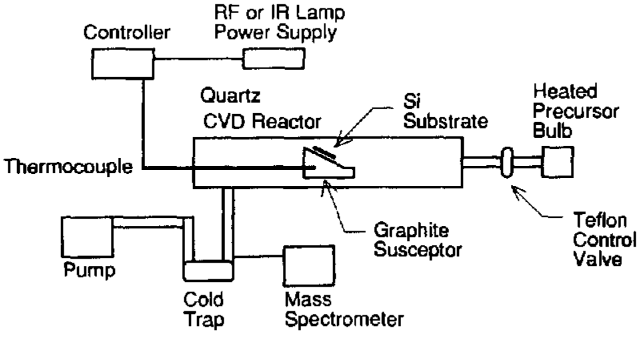

Fig. 1.

deposition and maintained at approximately 0.01–0.1 torr during the deposition by manually controlling the precursor inlet rate with a Teflon valve. The precursor compounds were contained in glass vessels that were heated to 90°C for **2**–**4** or maintained at ambient temperature for **1**. Volatile products of the reactions were characterized *in situ* by mass spectroscopy (Dycor Model MA200). The volatile products were also collected in a liquid nitrogen cooled trap and subsequently extracted with d_6-benzene for analysis by nuclear magnetic resonance (NMR) spectroscopy. NMR spectra were recorded on an IBM NR80 Fourier transform spectrometer (^{1}H NMR at 80.13 MHz) and a Bruker AMX-400 spectrometer. Ethylene was identified by the peaks at 28, 27, and 26 amu in the mass spectrum and its sharp ^{1}H NMR resonance at δ 5.25. Isobutene was identified by the peaks at 56, 55, 41 and 39 amu in the mass spectrum and its characteristic ^{1}H NMR resonances at δ 4.73 (septet, 1.2 Hz), 1.59 (triplet, 1.2 Hz). Trimethylsilane was identified by the peaks at 74, 73, and 59 amu in the mass spectrum and ^{1}H NMR resonances at δ 4.15 (decet, 3.7 Hz) and δ 0.00 (doublet, 3.7 Hz). Hydrogen was identified by the mass spectral peak at 2 amu. The relative atomic composition of the films was determined by Auger electron spectroscopy (AES) on a PHI 600 scanning Auger microscope.

3. Results and discussion

Compound **1** is a monomeric liquid with sufficient vapor pressure for room temperature CVD whereas the dimeric solids **2**–**4** required heating to 90°C. Table 1 summarizes the results of the CVD experiments. Thin films were deposited on Si substrates at 300–850°C using precursors **1**–**3**, while no film formed using **4**. In general, film growth temperatures were chosen to be in

TABLE 1. Results of pyrolysis study.

Compound	Pyrolysis temperature, °C	Film composition [a]	Major products observed by mass spectroscopy [b]	Major products observed by ^{1}H NMR [b]
Et$_2$BP(t-Bu)$_2$ **1**	550 850 [c]	BP$_{0.3}$C$_{0.7}$ BP$_{0.25}$C$_7$	hydrogen ethylene isobutene	ethylene isobutene
[Me$_2$BP(t-Bu)$_2$]$_2$ **2**	650 825 [d]	BP$_{0.2}$C$_2$ BC$_4$	hydrogen isobutene	isobutene
[Et$_2$BP(SiMe$_3$)$_2$]$_2$ **3**	600 850 [e]	BP$_{0.5}$C$_{1.4}$Si$_{0.9}$ BP$_{0.3}$C$_{3.5}$Si$_2$	hydrogen ethylene trimethylsilane	ethylene trimethylsilane other unidentified methylsilane compounds
[Me$_2$BP(SiMe$_3$)$_2$]$_2$ **4**	430 650	No film formed	hydrogen dimethylboron compound [f] trimethylsilyl compound [g]	methyl boron compound [f] bis(trimethylsilyl) phosphine [g]

[a] Determined by Auger electron spectroscopy. Estimated accuracy ±20%, relatively.

[b] All listed products were observed at both temperatures.

[c] At 850°C additional minor products appeared to be methane (16, 15 amu), acetylene (26, 25, 24 amu), isobutane (43 amu, ^{1}H NMR δ 0.86 (d, 6 Hz)), and tetramethylbutane (57 amu, ^{1}H NMR δ 0.85 (s)).

[d] AT 825°C additional minor products appeared to be methane (16, 15 amu) and isobutane (43 amu, ^{1}H NMR δ 0.86 (d, 6 Hz)).

[c] At 850°C additional minor products appeared to be methane (16, 15 amu), acetylene (26, 25, 24 amu, ^{1}H NMR δ 1.35 (s)), and ethane (30 amu, ^{1}H NMR δ 0.79 (s)).

[f] The mass spectral base peak at 41 amu is attributed to Me$_2$B$^+$, while the ^{1}H NMR spectrum shows a broad peak at δ 0.72 attributed to a methyl boron compound.

[g] Mass spectral peaks at 73 and 59 amu are attributed to a trimethylsilyl compound. ^{1}H NMR attributed to HP(SiMe$_3$)$_2$: δ 1.47 (d, 13.9 Hz), 0.08 (d, 6.9 Hz).

the range where the reagents are efficiently pyrolyzed (above 400°C), including temperatures near 850°C where BP has been deposited from B_2H_6 and PH_3 [4] in case this temperature is required to form the BP phase. Chemically resistant films also deposited on the reactor walls. They were unaffected by KOH in ethanol and reacted slowly and incompletely with boiling aqua regia. The films on Si were uniform and featureless as observed by scanning electron microscopy. Auger analysis showed considerable carbon ($C/B = 0.67–7$) and a deficiency in phosphorus ($P/B = 0–0.5$). Higher deposition temperatures lead to increased carbon incorporation and to increasing phosphorus deficiency, as has been observed in other III–V systems [7]. At 850°C mainly carbon and boron films deposited with a composition similar to that of a BC_3 material obtained from BCl_3 and benzene at 800°C [8,9].

Only the stable volatile products of the reactions were observed by mass spectroscopy and NMR, and they do not always account for mass balance in the deposition reactions. Therefore, we will restrict ourselves to a qualitative analysis using the major products observed as clues to the major decomposition pathways. Two reaction pathways, β-hydrogen elimination and homolytic bond fission, are sufficient to explain the major products observed in this study.

The principal gaseous species observed by mass spectroscopy during the deposition reaction using **1** were ethylene and isobutene. Addition of H_2 carrier gas at 0.1–1 torr did not significantly alter the hydrocarbon products. At lower pyrolysis temperatures ($\leq$ 200°C), larger amounts of ethylene relative to isobutene were observed, indicating preferential loss of ethylene from **1**. Compound **1** also appears to lose ethylene slowly at room temperature when kept at a low pressure for an extended period. NMR spectroscopic analysis indicates that this product is an unsymmetrical dimer, $[Et(H)BP(t\text{-}Bu)_2][Et_2BP(t\text{-}Bu)_2]$ [10 *]. Alkene elimination from boron is consistent with the reported decomposition of $(t\text{-}Bu)_2BP(t\text{-}Bu)_2$ to form $[i\text{-}Bu(H)BP(t\text{-}Bu)_2]_2$ at 0°C [11]. Elimination of ethylene from **1** is essentially a dehydroboration reaction of an alkylborane that has a low activation energy [12].

With the available data it is not possible to unequivocally determine how the t-Bu groups on phosphorus are eliminated. However, at the low pressure conditions used in these studies, and in view of Stringfellow's results [13] on the pyrolysis of $t\text{-}BuPH_2$, homolytic formation of t-Bu radicals and subsequent conversion to isobutene may be more likely than a β-hydrogen elimination process.

Since **1** did not form carbon-free boron phosphorus films, compounds **2**–**4** were examined where alkene elimination from boron or phosphorus was avoided by using methyl or trimethylsilyl groups, respectively. With **2** the major gaseous product is isobutene, while **3** gave ethylene, trimethylsilane, and smaller amounts of other methylsilane compounds. The absence of any significant amounts of coupled products (neopentane from **2** or $EtSiMe_3$ from **3**) from a concerted elimination pathway indicates that β-hydrogen elimination or homolytic bond fission again account for the observed products. The presence of significant amounts of Si in films formed from **3** indicates that the phosphorus substituents are a major source of carbon impurity. For films grown from **2** the methyl groups on boron probably also contribute to carbon in the films, since no major volatile product was observed that accounted for elimination of the methyl group.

Compound **4** was prepared in the hopes of producing BP by $SiMe_4$ elimination by analogy to the formation of InP from $[Me_2InP(SiMe_3)_2]_2$ [14]. The pyrolysis of **4** did not produce any film. The observed products, a dimethylboron compound and $HP(SiMe_3)_2$, are consistent with efficient initial homolysis of the boron–phosphorus bond. Thus, the desired $SiMe_4$ elimination pathway is too high in energy compared to the B–P bond strength.

4. Conclusions

The decomposition pathway of the phosphinoborane compounds depends strongly on the nature of the substituents on boron and phosphorus. β-hydrogen elimination of alkene from boron is a preferred reaction pathway, while concerted elimination reactions appear to be inefficient for these compounds. Significant carbon incorporation occurs from all precursors via an unidentified reaction pathway. Preferential loss of phosphorus occurs under these low pressure conditions and is nearly complete at higher pyrolysis temperatures that favor formation of carbon-rich films. Although these phosphinoborane compounds do not appear to be suitable precursors for pure boron phosphide, the B-P-C films obtained are chemically inert and may be of interest as protective coatings.

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* Reference number with asterisk indicates a note in the list of references.

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10 A colorless crystalline product was isolated from samples of **1** after prolonged storage under vacuum. NMR analysis in d_8-toluene was consistent with a formulation of $[\mathrm{Et(H)BP(t\text{-}}Bu)_2]$ $[\mathrm{Et_2BP(t\text{-}Bu)_2}]$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR δ 23.57 (s). $^{11}\mathrm{B}\{^1\mathrm{H}\}$ NMR δ 6.59 (br, s), -18.05 (t, $^1J_{B-P} = 53$ Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: three equal peaks for ethyl CH_3 at δ 11.19 (t, 9.4 Hz), 11.44 (t, 8.4 Hz), 17.09 (t, 7.8 Hz); CH_2 at δ 11.9 (br), 12.3 (br), 9.2 (br); t-Bu resonances at δ 33.54 (s), 32.02 (s), 37.73 (t, 7.6 Hz), 32.05 (t, 15.1 Hz). ^{1}H NMR ethyl CH_3 resonances at δ 1.00 (t, 7.4 Hz), 1.06 (t, 7.3 Hz), 1.23 (t, 7.5 Hz); CH_2 at δ 1.33 (m), 1.20 (m), 1.05 (m); hydride resonance at δ 2.66 (m, br); t-Bu resonances at δ 1.39 (t, 4.9 Hz), 1.37 (t, 5.0 Hz). The overlapping ethyl resonances were identified with the aid of two-dimensional NMR.

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