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Chemical Vapor Deposition of Metal Borides, 4: The Application of Polyhedral Boron Clusters to the Chemical Vapor Deposition Formation of Gadolinium Boride Thin-film Materials

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The chemical vapor deposition of high-quality polycrystalline thin films of gadolinium hexaboride, GdB_6, was achieved through the vacuum copyrolysis of gas-phase boron hydride clusters, such as *nido*-pentaborane(9) [B_5H_9] and *nido*-decaborane(14) [$B_{10}H_{14}$], and gadolinium(III) chloride. These films typically displayed deep blue colors, were very hard and adhered very well to most deposition substrates. Depositions were carried out on a variety of substrates including quartz, copper, silicon, SiO_2 and ceramic materials. X-ray diffraction and scanning electron microscopic data showed the formation of highly crystalline materials with a strongly preferred orientation in the (111) direction. Attempted depositions of gadolinium boride films on CaF_2(111) resulted in the apparent formation of a ternary (Ca/Gd)B_6 phase in which the calcium is presumably substituted for gadolinium atoms in the cubic GdB_6 structure. The gadolinium boride thin films were investigated by scanning electron microscopy (SEM), X-ray emission spectroscopy (XES), X-ray diffraction (XRD), and glow-discharge mass spectrometry (GDMS). GDMS showed that the GdB_6 films were relatively uniform in composition in the bulk material.

Keywords: chemical vapor deposition; thin films; gadolinium hexaboride; X-ray diffraction; X-ray emission spectroscopy; scanning electro microscopy; mass spectrometry

INTRODUCTION

Rare-earth metal borides are materials of particular technological interest due to their refractory, magnetic and electric properties.[1] These metal borides often possess metallic conductivities, some with conductivities significantly higher than the constituent metal itself, and most are excellent thermionic materials. The lanthanide borides are structurally unique in the solid state since they typically consist of covalently bonded boron polyhedra surrounding the metal atoms. Thus, the rare-earth metals, unlike many of the transition metals, tend to form boron-rich borides preferentially to metal-rich phases. The strong multicenter, covalent bonding of these boron polyhedra is believed to impart the observed high stability, hardness and high melting points to these metal borides.[2] Gadolinium boride is an excellent magnetic material and is one of the strongest magnets among the binary metal borides.

Metal borides have been prepared by a variety of methods but synthetic techniques typically have employed high temperatures (above 1000 °C) and low-volatility precursors, such as metal oxides and boron carbide.[3] Because of the high temperatures required and the refractory nature of the rare-earth borides, pure metal boride materials have been difficult to prepare. A systematic and general method for depositing thin films of metal borides has, however, not been previously reported.

Chemical vapor deposition (CVD) technology has recently been shown to be one of the most effective methods for the deposition of pure thin-film mateials.[4,5] The use of discrete metallaboranes as single-source precursors seems to be a logical choice, but metallaborane compounds are often air-sensitive, difficult to synthesize and purify in reasonably large quantities (>100 mg), and relatively difficult to handle (occasionally even thermally unstable and pyrophoric).[6] The CVD of metal boride films from several metallaborane

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precursors has recently been reported.[7,8] The deposition of these films, however, typically lacked sufficient compositional control and the deposited materials were either amorphous or crystallized only after prolonged annealing. In addition, loss of boron from the precursor during the CVD process, incorporation of impurities such as oxygen and carbon, and the generation of pyrophoric by-products, such as diborane, were frequently observed. These factors make the single-source precursor route much less attractive for CVD of metal borides.

There are no reports of the chemical vapor deposition (CVD) of gadolinium boride thin films. The synthesis of bulk gadolinium boride phases, such as GdB_4 and GdB_6, from a molecular precursor, $Gd_2(B_{10}H_{10})_3$, at 1000–1200 °C has, however, been recently reported.[9] Thus, powders containing both the gadolinium borides and amorphous boron have been obtained as products from the thermolysis of the molecular precursor $Gd_2(B_{10}H_{10})_3$.[9]

In this work, we report the results of our investigations into the formation and characterization of gadolinium boride thin films using chemical vapor deposition from readily obtainable and easily handled rare-earth metal salts and polyhedral borane clusters.

EXPERIMENTAL

Physical measurements

FT-IR spectra in the range 400–4000 cm^{-1} were measured on a Mattson Galaxy 2020 spectrometer and were referenced to the 1601.8 cm^{-1} band of polystyrene. All compounds were recorded as Nujol mulls sandwiched between NaCl plates.

Scanning electron micrographs (SEM) were obtained on an ETEC autoscan instrument in the N. C. Brown Center for Ultrastructure Studies of the SUNY College of Environmental Science and Forestry, Syracuse, NY, USA. Photographs were recorded on either Kodak Ektapan 4162 or Polaroid P/N 55 film.

X-ray emission spectra (XES) were obtained on a Kevex 7500 Microanalyst System. The X-ray diffraction patterns (XRD) were recorded on a Phillips APD 3520 powder diffractometer equipped with a PW 1729 X-ray generator and a PW 1710 diffractometer control system. Copper K_α radiation and a graphite single-crystal monochromator were employed in the measurements reported here.

The mass spectra were obtained on a VG 9000 glow discharge mass spectrometer using a 1 Torr argon discharge at 1 kV. The mass-spectral analyses were performed by Shiva Technology, Inc., Clay, NY, USA.

Materials

All solvents used were of reagent grade or better; after appropriate drying, they were degassed by repeated freeze–evacuate–thaw cycles and finally stored *in vacuo* prior to use.[10] *nido*-Decaborane(14), $B_{10}H_{14}$, was purchased from the Callery Chemical Company and was purified by vacuum sublimation before use. *nido*-Pentaborane(9), B_5H_9, was taken directly from our laboratory stock. The anhydrous (99.9%) $GdCl_3$ was commercially available (Cerac, Inc.) and was used as received.

Chemical vapor deposition (CVD) of gadolinium boride

The CVD depositions were performed using a medium–high-vacuum quartz reactor tube apparatus (1×10^{-6} Torr ultimate vacuum) employing a tube of 10 mm o.d. with a length of 60 cm. The apparatus was equipped with a chromel–alumel thermocouple with the thermocouple junction placed close to the tube in the middle of the oven. The reactor tube was placed horizontally in a tube furnace and was heated using an external electrical resistance furnace. The overall experimental operation of the reactor employed here was similar to that previously described.[11] In a typical experiment, 1.0 g (3.8 mmol) of anhydrous (99.9%) gadolinium(III) chloride was placed in a quartz boat with the deposition substrates suspended over the top of the boat. The boat and substrates were then placed in the deposition system using inert atmosphere techniques.[10] The entire reactor system was evacuated to 4×10^{-6} Torr at room temperature for at least 2 h prior to deposition. A boron precursor reservoir containing either freshly sublimed *nido*-decaborane(14), $B_{10}H_{14}$, or vacuum-distilled *nido*-pentaborane(9), B_5H_9, was connected to the reactor. The borane reservoir flask was maintained at a constant temperature during the entire experiment by use of an external temperature bath jacketing the reservoir flask [22–28 °C for decaborane(14) and −78 °C for pentaborane(9)]. Control of the boron precursor flow into the reaction system was achieved through the use of narrow-bore Teflon vacuum stopcocks (0–4 mm) and by adjusting the temperature of the precursor flask by using an external constant-temperature bath to modify its vapor pressure.[10] The reactor was then slowly heated to 850 °C under dynamic vacuum. After a stable temperature had been obtained, the Teflon valve to the borane reservoir flask was opened to allow borane vapor to pass over the hot $GdCl_3$ while under dynamic vacuum conditions. The unreacted borane and other reaction by-products were trapped downstream in a trap cooled by liquid nitrogen. The deposition was continued for 3 h, during which time a film coated both the walls of the reactor and the deposition substrates held above the $GdCl_3$ boat. The stopcock to the borane flask was then closed and the reactor was allowed to cool slowly to room temperature. The reactor was filled with dry nitrogen and the film was removed from the system for further study. The GdB_6 films thus prepared typically had velvet-like appearances and were very hard but rather brittle.

RESULTS AND DISCUSSION

The chemical vapor deposition of very high-quality solid-state thin films of gadolinium hexaboride, GdB_6, was readily achieved through the vacuum copyrolysis of gas-phase borane hydride clusters and gadolinium(III) chloride. This deposition process was found to occur at significantly lower temperatures than had been previously reported for the formation of the closely related LaB_6 films which were formed from a complex mixture of precursors that presumably involved BCl_3 and $LaCl_3$ as the active gas-phase species.[12] The formation of gadolinium boride thin-film materials by CVD techniques has not, however, been previously reported. The GdB_6 films were formed both on the substrates suspended above the $GdCl_3$ reservoir boat and on the walls of the reactor in the hot zone. Films were formed on a variety of substrates including quartz, copper, silicon, SiO_2 and ceramic materials. These films typically displayed a deep blue color, were very hard, and frequently possessed a velvet-like surface appearance. The films also adhered very well to most deposition substrates. It was also possible, although rather difficult, to obtain substrate free films by scraping the deposits from the walls of the reactor. As described below, the films were found to be composed of beautifully formed, highly crystalline materials. Film thicknesses could be readily varied by modifying the flow rate of the volatile borane precursor into the reactor and by changing the overall time and temperature of the deposition reactions. The as-deposited films were typically studied by a variety of techniques including scanning electron microscopy (SEM), X-ray emission spectroscopy (XES), X-ray diffraction (XRD) and glow discharge mass spectrometry (GDMS).

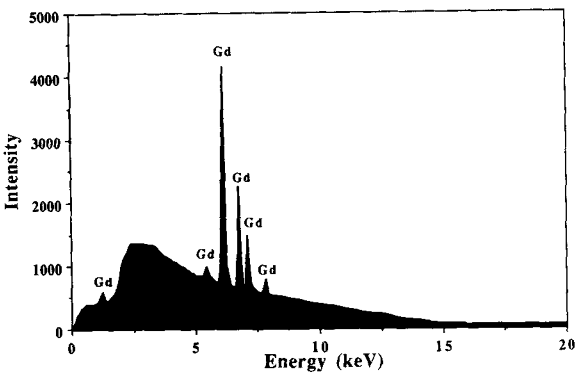

Figure 1 A typical X-ray emission (XES) spectrum of a GdB_6 film. The film was deposited from gadolinium(III) chloride and *nido*-pentaborane(9), B_5H_9, at 863 °C on a quartz substrate.

Gadolinium boride thin films were readily prepared by employing either *nido*-pentaborane(9), B_5H_9, or *nido*-decaborane(14), $B_{10}H_{14}$, clusters as the boron-containing precursor. As mentioned previously,[11] *nido*-pentaborane(9) is more easily controlled in a flow system because of its higher vapor pressure ($\text{v.p.}_{(25\,°\text{C})} = 209\ \text{Torr}$)[13a] while *nido*-decaborane(14) is more easily handled since it is an air-stable material at room temperature ($\text{v.p.}_{(60\,°\text{C})} = 1\ \text{Torr}$).[13b, c, 14] Depositions with either of these clusters gave very similar thin-film results.

A typical X-ray emission spectrum (XES) of a gadolinium boride film prepared from gadolinium(III) chloride and *nido*-pentaborane(9) is shown in Fig. 1. The XES analysis of the film showed intense signals due only to gadolinium at 1.185 keV (M_α), 5.326 keV (L_l), 6.059 keV (L_α), 6.714 keV ($L_{\beta 1}$), 7.102 keV ($L_{\beta 2}$) and 7.788 keV (L_γ). The presence of chlorine impurities in the film were not detected in the XES data.

Scanning electron microscopy (SEM) provided a clearer picture of the morphology and structure of the CVD-deposited gadolinium boride thin films. A representative SEM image of a blue gadolinium boride film deposited from gadolinium(III) chloride and *nido*-pentaborane(9) is shown in Fig. 2(a). The morphology of the film showed very well-formed crystalline grains of uniform shape. The grain sizes of these cubic GdB_6 crystallites typically varied from 1 to 4 μm. The distribution of the crystallite sizes was dependent upon the rate and temperature of deposition, as anticipated.[4] The crystals appeared to be growing perpendicular to the substrate surface and the deposited material was found to be very conformal without any significant void formation. This complete conformal coverage of the substrate is probably due to the sufficiently high surface mobilities of the deposited material at the CVD temperatures employed. Lower-temperature CVD processes for other metallic boride films, such as nickel and aluminium boride,[11,15] frequently show the formation of surface voids, presumably because of the insufficient surface mobilities of the metal borides at the lower deposition temperatures. The absence of voids in the gadolinium boride materials formed at the temperatures employed here (approximately 850 °C) is somewhat surprising, however, since this deposition temperature is significantly below the melting point of the pure material (m.p.>2100 °C).[1] Other materials formed by CVD processes at temperatures significantly below the melting point of the pure material often show significant void formation, presumably by a shadowing mechanism coupled with insufficient surface mobility effects.[16]

X-ray diffraction (XRD) data for films deposited on quartz substrates, coupled with the SEM data presented above, clearly showed that the materials were highly crystalline cubic GdB_6. A typical XRD pattern for these materials is presented in Fig. 3 and the data are summarized in Table 1. The observed XRD data, when compared with the reported XRD data for a randomly oriented polycrystalline GdB_6 sample (Table 1), show a strongly preferred orientation in the (111) direction for the CVD-deposited material. The preferred orientation in our deposited GdB_6 materials was observed, however, only when the films were deposited on quartz substrates and not on the copper of ceramic substrates. Since the orientation and morphology of the CVD-deposited films seemed to be strongly surface-dependent, attempts were made to deposit single- or other preferred-orientation films by using single-crystalline substrates with good lattice-matching properties to cubic GdB_6. A single-crystalline magnesium oxide (200) substrate was initially chosen since this material is relatively inert and

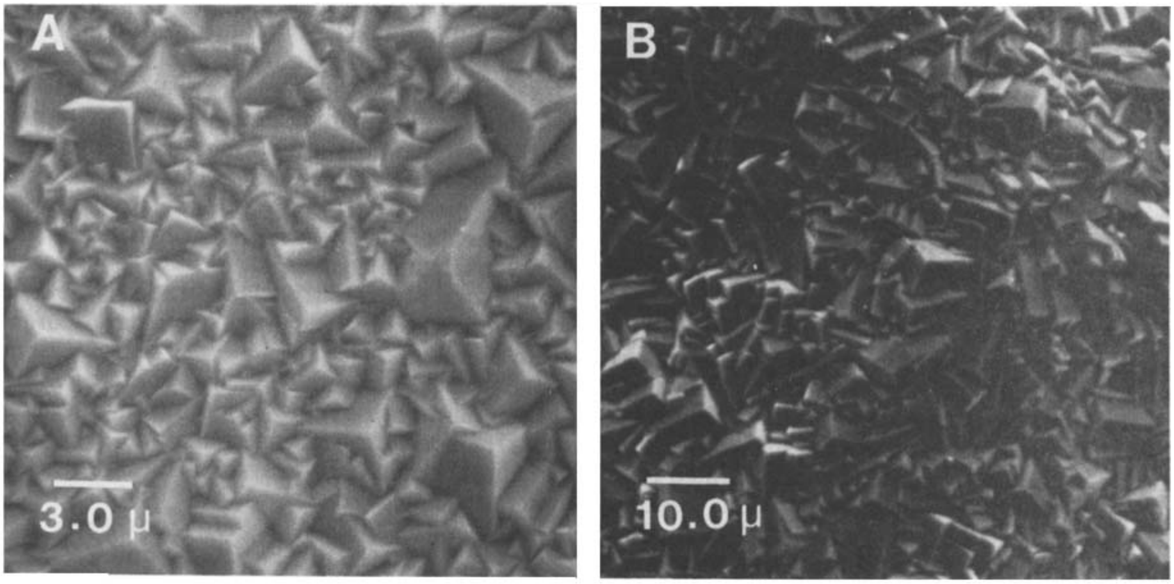

Figure 2 Scanning electron micrographs (SEM) of deposited gadolinium boride films. (a) A GdB_6 film deposited from $GdCl_3$ and *nido*-B_5H_9 at 863 °C on a quartz substrate (3300× magnification). (b) $(Ca/Gd)B_6$ film obtained from the deposition of a gadolinium boride film in the presence of a CaF_2 substrate (1100× magnification). The film was deposited from $GdCl_3$ and B_5H_9 at 850 °C with a $CaF_2(111)$ substrate.

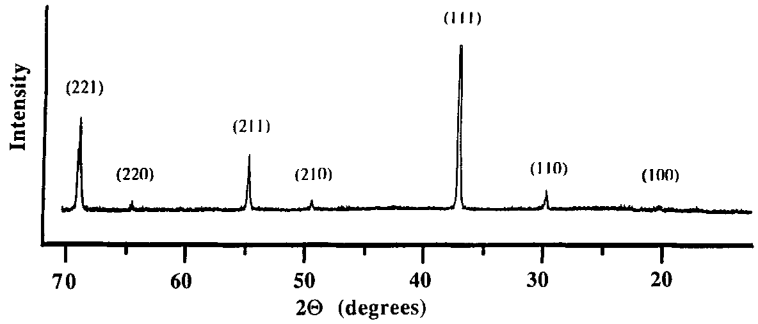

Figure 3 X-ray diffraction pattern (XRD) of a typical cubic GdB_6 film deposited on a quartz substrate from gadolinium(III) chloride and *nido*-pentaborane(9) at 863 °C (*hkl* indices are given above each peak in parentheses).

displays only a 2.2% lattice mismatch with GdB_6 (a for $GdB_6 = 4.108$ Å).[1,18] This small mismatch was not anticipated to present significant problems for GdB_6 monolithic thin-film formation. When the films were deposited on the MgO(200) substrates, the observed materials were light blue and displayed very fine microstructures which were not clearly resolved in the SEM analysis. The XES data showed signals due to both gadolinium and magnesium (from the substrate), with no chlorine detected. The XRD patterns for these films were, however, very complex and exhibited numerous lines. The XRD data indicated that magnesium borides, gadolinium borides or mixed-metal ternary borides were formed on the substrate. Since reflections due to the (200) planes were absent in the XRD pattern of the CVD GdB_6 films grown on quartz substrates (Fig. 3 and Table 1), it is possible that the use of MgO(200) substrates provided an incompatible lattice orientation for effective GdB_6 growth.

Table 1 X-ray diffraction (XRD) data for a cubic gadolinium hexaboride film, GdB_6, deposited from gadolinium(III) chloride and *nido*-pentaborane(9) at 863 °C on a quartz substrate

		Relative intensity[a]	
d spacing (Å)	(*hkl*)	Observed[b]	JCPDS File
4.09	(100)	3	65
2.90	(110)	12	100
2.37	(111)	100	55
2.05	(200)	0	35
1.83	(210)	7	60
1.67	(211)	23	35
1.45	(220)	4	10
1.37	(221)	41	35

[a] The observed intensities are compared with reported intensities for a randomly oriented cubic GdB_6 sample.[17]
[b] matches JCPDS File No. 24-1082, XRD data for GdB_6.[17]

Since the as-deposited GdB_6 films on quartz substrates showed a strongly preferred orientation in the (111) direction, CaF_2(111) was investigated as a possible substrate to determine whether this orientation of the substrate would facilitate preferential GdB_6(111) growth. Calcium fluoride is also a relatively inert material with a small lattice mismatch with cubic GdB_6. When the CVD formation of gadolinium boride was attempted on the CaF_2(111) substrates, however, it was observed that the substrate apparently disappeared from its original location and a blue film was again formed on the walls of the reactor during the deposition. The XES analysis of the deposited material, given in Fig. 4, showed that the calcium from the substrate was incorporated into the film deposited on the walls of the reactor. Intense signals due to gadolinium were again detected at 1.185 keV (M_α), 5.326 keV (L_l), 6.059 keV (L_α), 6.714 keV ($L_{\beta1}$), 7.102 keV ($L_{\beta2}$) and 7.788 keV (L_γ) while a signal due to calcium was detected at 3.690 keV (K_α). Chlorine conta-

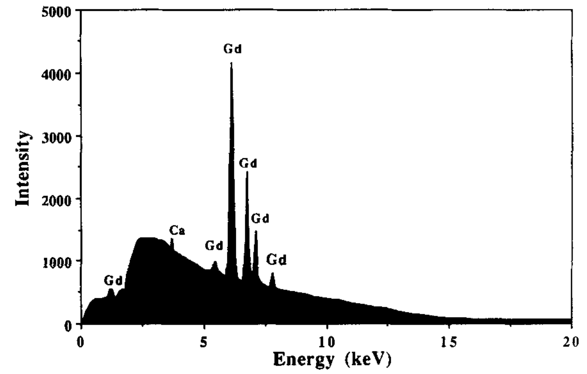

Figure 4 An X-ray emission spectrum of a $(Ca/Gd)B_6$ film. The film was obtained from the walls of the reactor from the copyrolysis of gadolinium(III) chloride and *nido*-pentaborane(9) at 850 °C with a CaF_2(111) substrate.

mination also was not observed in the XES data. The SEM microstructure of the resultant (Ca/Gd)B_6 film, shown in Fig. 2(b), was different from that previously observed for the pure cubic GdB_6 films [Fig. 2(a)]. Since cubic CaB_6 ($a = 4.144$ Å) and GdB_6($a = 4.114$ Å) are isostructural and have very similar lattice parameters, it is possible that the substitution of gadolinium atoms by calcium atoms in the GdB_6 crystals could form a ternary (Ca/Gd)B_6 phase. In a control experiment using similar deposition conditions but employing only the CaF_2(111) and pentaborane(9) without $GdCl_3$, no deposition reaction was observed and the CaF_2(111) substrate was recovered intact at the end of the experiment. Similarly, no reaction was observed when CaF_2(111) and $GdCl_3$ were copyrolyzed under identical conditions without pentaborane(9). These observations provide support for the idea that a reaction occurred between the depositing GdB_6 film and the CaF_2 substrate which led to the disappearance of the CaF_2 and incorporation of calcium into the film. When other single-crystalline surfaces, such as Si(100), Si(111) or SiO_2 grown on Si(111), were investigated as possible preferred-orientation substrates, only amorphous rather than crystalline films were obtained. These films were typically gray and did not show a clear XRD pattern. The color of the films suggests that the materials were either amorphous GdB_2 or GdB_4 phases. This is in distinct contrast to the experiments with quartz substrates in which highly crystalline blue cubic GdB_6 films were readily deposited. These observations again indicate that the formation of GdB_6 is rather substrate-dependent. Such substrate dependence of CVD reactions is well known for a variety of other systems,[4,19] including those encounters in our previous work with the CVD formation of nickel boride in which the formation of the metastable Ni_7B_3 phase was observed only on GaAs surfaces.[11]

The elemental depth profile (composition) of gadolinium boride pyrolytically deposited from gadolinium(III) chloride and borane clusters was determined by glow-discharge mass spectrometric analyses (GDMS). A plot of the elemental film composition as a function of sputtering time (depth) was constructed from a series of mass spectra recorded while the sample was being Ar^+-etched. A GDMS depth profile for a typical sample is shown in Fig. 5. The surface of the film was found to contain approximately 66 wt% boron and 34 wt% gadolinium. The bulk material, however, was found to contain about equal weight-percentages of both boron and gadolinium, corresponding to a calculated bulk composition of approximately GdB_{14} (GdB_6 and B). The data also showed that the composition of the bulk film was relatively uniform and was not significantly contaminated with chlorine. The lower gadolinium content at the surface of the film is probably due to a depetion of the gadolinium(III) chloride from the source reservoir and also, therefore, from the gas phase during the reaction. A second possible explanation for the observed gadolinium content reduction is that the surface of the gadolinium(III) chloride reservoir becomes contaminated with a refractory layer of either gadolinium boride or native boron. As this source-reservoir blanketing increases, the relative gadolinium(III) chloride concentration in the gas phase again decreases as smaller portions of the reservoir are left uncontaminated. This surface contamination has been observed experimentally in the higher-temperature ranges as a black layer coating the surface of the reservoir. Since the gas-phase boron concentration is essentially constant throughout the deposition process, a relative depletion of the gas-phase gadolinium species as the experiment progresses would be expected. The decreased gas-phase concentration of the $GdCl_x$ species as the reaction proceeds would be expected to lower the gadolinium concentration in the films and to cause greater boron incorporation into the top layers of the film. The very small amounts of chlorine detected in the film may arise

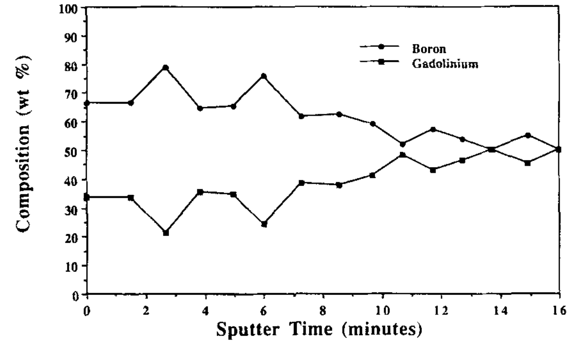

Figure 5 A plot of a typical gadolinium boride thin-film composition as a function of film thickness as obtained by glow discharge mass spectrometry (GDMS). The depth profile was constructed from a series of glow-discharge mass spectra recorded while the sample was being Ar^+-sputtered (the etching rate was approximately 0.05 μm min^{-1}). The gadolinium boride film was deposited from gadolinium(III) chloride and *nido*-pentoborane(9) at 850 °C on a ceramic substrate.

from a trapping of pyrolyzed $GdCl_x$ species on the porous ceramic substrate employed, similar to that proposed for $LaCl_3$ in the CVD formation of LaB_6.[20] Dissociation of $GdCl_3$ around 700 °C into $GdCl_2$ (100% relative intensity), GdCl (23%) and Gd (39%) has been reported in a mass-spectrometric study.[21]

The pyrolysis of boranes at 50–250 °C has been studied previously[4, 15, 22] and, although many groups have investigated the pyrolysis of these species, the pyrolysis of *nido*-pentoborane(9)[23] and *nido*-decaborane(14) is not fully understood.[24] During pyrolysis, boranes are rapidly converted to other boranes and hydrogen.[22–24] In addition, non-volatile and air-sensitive solid BH_x polymers are also typically formed. It is possible that, in our CVD reactions, such polymeric solids may play an important role in the CVD of metal borides through a variety of complex surface reactions. Boranes also typically liberate hydrogen *in situ* during thermal reactions which can facilitate the abstraction of chlorine from metal halides under CVD conditions to form activated gas-phase precursor species.[25] We are currently pursuing detailed investigations employing both mass-spectroscopic and multinuclear NMR techniques to determine the nature of the volatile gas-phase products formed during the CVD process. Preliminary data suggests that HCl, BCl_3 and fused cage borane species, among others, are formed during the thermal CVD reactions.

CONCLUSIONS

It appears that excellent-quality polycrystalline GdB_6 films can be readily prepared from the CVD of gadolinium(III) chloride and borane clusters at relatively low temperatures. The gadolinium boride films formed from the metal chloride salts contained very little, if any, contamination. These experiments indicate that the CVD formation of solid-state borides from metal halides and borane cluster precursors may provide a general, inexpensive and versatile new route to these technologically important materials.

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REFERENCES

1. B. Post, in: *Boron, Metallo-Boron Compounds and Boranes*, Adams, R. M. (ed.), Interscience, New York, 1964, Chapter 5.4.
2. R. W. Johnson and A. H. Daane, *J. Phys. Chem.* **65**, 909 (1961).
3. N. N. Greenwood and A. Earnshaw, *Chemistry of The Elements*, Pergamon, Oxford, 1985.
4. J. T. Spencer, *Prog. Inorg. Chem.* **41**, 145 (1994).
5. (a) P. A. Dowben, J. T. Spencer and G. T. Stauf, *Mat. Sci. Eng.* **B2**, 297 (1989). (b) M. R. Leys, *Chemtronics* **2**, 155 (1987). (c) G. J. Davies and D. A. Andrews, *Chemtronics* **3**, 3 (1988). (d) A. C. Jones, J. S. Roberts, P. J. Wright, P. E. Oliver and B. Cockayne, *Chemtronics* **3**, 152 (1988).
6. R. N. Grimes, in: *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A. and Abel, E. (eds), Pergamon, Oxford, 1982, Chapter 5.5.
7. (a) M. M. Amini, T. P. Fehlner, G. J. Long and M. Politowski, *Chem. Mater.* **2**, 432 (1990). (b) B. H. S. Thimmappa, T. P. Fehlner, G. J. Long and O. A. Pringle, *Chem. Mater.* **3**, 1148 (1991). (c) C. S. Jun, T. P. Fehlner and G. J. Long, *Chem. Mater.* **4**, 440 (1992).
8. J. A. Jensen, J. E. Gozum, D. M. Pollina and G. A. Girolami, *J. Am. Chem. Soc.* **110**, 1643 (1988).
9. H. Itoh, Y. Tsuzuki, T. Yogo and S. Naka, *Mater. Res. Bull.* **22**, 1259 (1987).
10. D. F. Shriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, Wiley–Interscience, New York, 1986.
11. S. Kher and J. T. Spencer, *Chem. Mater.* **4**, 538 (1992).
12. (a) Q. Jang, R. LaFerla, R. B. Kaplan, B. S. Ahern and D. W. Weyburn, *5th Int. SAMPE Conf.* 468 (1991). (b) A. Hagimura and A. Kato, *Nippon Kagaku Kaishi* **7**, 1108 (1980).
13. (a) H. E. Wirth and E. D. Palmer, *J. Phys. Chem.* **60**, 914 (1956). (b) D. T. Hurd and M. M. Safford, US Patent 2 588 559, 26 June 1954. (c) M. M. Safford and D. T. Hurd, US Patent 2 558 561, 26 June 1954.
14. (a) E. L. Muetterties, *Boron Hydride Chemistry*, Academic Press, New York, 1975. (b) W. N. Lipscomb, *Boron Hydrides*, Benjamin, New York, 1963. (c) T. Onak, in: *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A. and Abel, E. (eds.), Pergamon, Oxford, 1982, Chapter 5.4.
15. (a) J. A. Glass, Jr, S. Kher and J. T. Spencer, *Thin Solid Films* **207**, 15 (1992). (b) J. A. Glass, Jr, S. Kher and J. T. Spencer, *Chem. Mater.* **4**, 530 (1992).
16. B. A. Movchan and A. V. Demchishin, *Fiz. Met.* **28**, 83 (1977).

17. Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, JCPDS File No. 24-1082.
18. M. A. Eich and P. W. Gilles, *J. Am. Chem. Soc.* **81**, 5030 (1959).
19. T. F. Mountziaris and K. F. Jensen, *J. Electrochem. Soc.* **138**, 2426 (1992).
20. S. S. Kher, Ph.D. Dissertation, Syracuse University, 1993.
21. S. Ciach, A. J. Nicholson, D. L. Swingler and P. J. Thistlethwaite, *Inorg. Chem.* **12**, 2072 (1973).
22. N. N. Greenwood, *Chem. Soc. Rev.* 49 (1992). (b) N. N. Greenwood and R. Greatrex, *Pure Appl. Chem.* **59**, 857 (1987). (c) R. Greatrex, N. N. Greenwood and C. D. Potter, *J. Chem. Soc.* 81 (1986). (d) A. J. Owen, *J. Appl. Chem.* **10**, 483 (1960). (e) L. H. Long, *J. Inorg. Nucl. Chem.* **32**, 1097 (1970). (f) M. Hillman, D. J. Mangold and J. H. Norman, *J. Inorg. Nucl. Chem.* **24**, 1565 (1962). (g) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.* **86**, 1012 (1964). (h) L. V. McCarty and P. A. Di Giorgio, *J. Am. Chem. Soc.* **73**, 3138 (1951). (i) A. C. Bond and M. L. Pinsky, *J. Am. Chem. Soc.* **92**, 32 (1970). (j) J. K. Bragg, L. V. McCarty and F. J. Norton, *J. Am. Chem. Soc.* **73**, 2134 (1951).
23. T. J. Houser and R. C. Greenhough, *Chem. Ind.* 323 (1967).
24. (a) A. J. Owen, *J. Chem. Soc.* 5438 (1961). (b) H. C. Beachell and J. F. Haugh, *J. Am. Chem. Soc.* **80**, 2939 (1958). (c) B. Siegel and J. L. Mack, *J. Phys. Chem.* **62**, 373 (1958).
25. T. M. Besman and K. E. Spear, *J. Electrochem. Soc.* **124**, 786 (1977).