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Chemical vapor deposition of metal borides: 6. The formation of neodymium boride thin film materials from polyhedral boron clusters and metal halides by chemical vapor deposition

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The chemical vapor deposition (CVD) of crystalline thin films of neodymium hexaboride (NdB_6) was achieved using either *nido*-pentaborane(9) or *nido*-decaborane(14) with neodymium(III) chloride on different substrates. The highly crystalline NdB_6 films were formed at relatively moderate temperatures (835 °C, ca. 1 μm/h) and were characterized by scanning electron microscopy, X-ray emission spectroscopy, X-ray diffraction and glow discharge mass spectrometry. The NdB_6 polycrystalline films were found to be pure and uniform in composition in the bulk material. Depositions using $CoCl_2$, $NdCl_3$ and B_5H_9 as the CVD precursors resulted in the formation of a mixture of NdB_6 and CoB phases, rather than the ternary phase. **Copyright © 2008 John Wiley & Sons, Ltd.**

Keywords: chemical vapor deposition; metal boride; neodymium boride; cobalt boride

Introduction

Among solid-state materials, the metal borides are remarkable due to a combination of unique compositional and structural features, physical properties and potential applications to a wide variety of technological problems.[1,2] The element boron not only readily combines with most metals, but frequently does so to form a series of binary compounds with up to eight different metal-to-boron ratios for any given metal. Metal borides are known with solid-state structures that range from essentially isolated boron atoms to boron–boron bonded chains, two-dimensional continuous networks and complex three-dimensional frameworks which extend throughout the entire crystal.[2a] The structure of neodymium hexaboride (NdB_6), shown in Fig. 1, is an example of this latter complex three-dimensional structural type, in which B_6 octahedra are arranged in a body-centered cubic lattice with the octahedra linked to the apices of other octahedra in all six directions, giving a rigid yet relatively open structure. The strong multicenter, covalent bonding of these boron polyhedra is believed to impart the observed high stability, hardness, and high melting points to most of the boride materials.[3] While it is not possible to account for the boride structures in simple bonding terms, it is generally believed that the metal center donates electrons to the boron units in the boron-rich compounds, such as NdB_6. In the case of NdB_6, the *closo*-boron octahedra require 14 valence electrons ($2n + 2$), of which 12 are provided by the boron atoms.[4] If the neodymium then provides two electrons to the cage, one 'free' valence electron should remain per metal center, making the material an excellent conductor. This analysis is consistent with Hall-effect, solid-state ^{11}B NMR and conductivity measurements on these materials.[5] Also supportive of this analysis is the fact that MB_6 materials that contain only divalent metal centers, such as the pure alkaline earth hexaborides, are insulators rather than conductors since no 'free' electrons remain on the metal centers for conduction.[2] Thus, the bonding description of NdB_6 may be thought to contain both delocalized covalent (within the B_6 polyhedra) and predominantly ionic bonding modes (between the polyhedra and the metal). The best electronic description of these materials, however, comes from a more complex molecular orbital treatment such as that recently presented by Hoffmann for Ta_3B_4.[6] Several metal boride epitaxial thin films, such as HfB_2, have recently been studied carefully by XPS and related techniques in efforts to probe the structures and properties of these materials.[7] The unique structural and electronic diversity of the metal borides continues to inspire both theoretical and synthetic investigations of these materials. Indeed, many books have been written about these solid-state materials in which the literature has been presented in detail.[2a,8]

The metal borides typically are very refractory materials, possessing high melting points, exceptional hardnesses and high thermal electric conductivities. For example, the diborides of Zr, Hf, Nd and Ta all have melting points well over 3000 °C, exceeding those of the pure parent metals.[9] One additional important characteristic property of metal borides is that they possess electrical conductivities of a metallic order, and several borides, such as LaB_6 and TiB_2, have electrical resistances very much lower than the corresponding pure metals (e.g. over five times lower for TiB_2).

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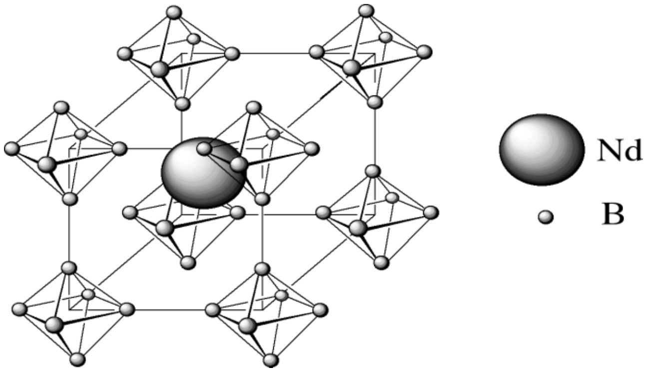

Figure 1. Structure of neodymium hexaboride.

The metal borides also exhibit enormous thermal stabilities and typically are not attacked by either dilute acids or bases or even concentrated mineral acids. Because of these properties, metal borides have found critical uses in a variety of applications, ranging from 'low technology' hard cutting surface coatings to advanced optoelectronic systems. The lanthanide metal borides, in particular, have recently become the center of interest not only because of their refractory, magnetic and electrical properties, but also from their potential use as excellent thermionic materials.[9b] Finally, these boride materials, owing to the very high thermal and high energy ($10^4 - 10^6$ eV) neutron capture cross sections of the ^{10}B nuclide, have been employed as neutron shields and in related 'nuclear-hardened' applications.

The synthesis of solid-state metal boride materials has employed a variety of preparative strategies.[2] All these methods, however, typically require very high temperatures (above 1000 °C) and employ the use of low-volatility precursors, such as metal oxides and boron or boron carbide, as shown in eqn (1).[10]

$$M_2O_3 + 15\ B \longrightarrow 2\ MB_6 + 3\ BO \qquad (1)$$

Because of the nature of these high-temperature techniques and the refractory nature of the rare earth borides themselves, pure metal boride materials have been difficult to both prepare and analyze. None of the traditional methods for preparing metal borides, however, may be in any sense termed general. In addition, these preparations have focused almost entirely on the formation of bulk materials, rather than on the technologically important and scientifically interesting formation of thin film materials.

Chemical vapor deposition (CVD) methods have recently been shown to be among the most effective methods for the deposition of pure, thin-film materials.[11,12] The chemical vapor deposition of thin films of metal borides, particularly the lanthanide borides, has previously presented significant challenges. The CVD of transition metal boride films from single-source metallaborane CVD precursors has recently been reported.[13,14] While the single source feature of this method is particularly attractive, the deposition of these films, however, has typically lacked sufficient compositional control and the deposited materials were either amorphous or crystallized only after prolonged annealing. In addition, metallaborane complexes are often rather difficult and time-consuming to prepare in pure form and in sufficient quantities for CVD applications.[15] While not a CVD process, the synthesis of bulk gadolinium boride phases, such as GdB_4 and GdB_6, from a single molecular precursor, $Gd_2(B_{10}H_{10})_3$, at 1000–1200 °C has also been reported.[16] In this report, powders containing both the gadolinium borides and amorphous boron were obtained as products from the thermolysis of the molecular precursor $Gd_2(B_{10}H_{10})_3$.[16] The chromium complex of the $B_3H_8^-$ species, $Cr(B_3H_8)_2$, has also been used as a CVD precursor to form chromium boride materials.[17]

Transition metal borohydride complexes, such as $Ti(BH_4)(dme)$, $Hf(BH_4)_4$, $V(BH_4)_2(dmpe)_2$ and $Zr(BH_4)_4$, have been reported as precursors in the CVD preparation of several metal boride thin films.[14,18,19] It appears that, when the metal coordination sphere is completed solely by borohydride ligands, metal boride films typically result.[14,19–21] When hydridometalborohydride complexes are used instead, such as $AlH_2(BH_4)_3{\cdot}2N(CH_3)_3$, very clean depositions of pure metal result.[20,21] The application of these precursors, however, is often severely limited by both the instability/reactivity and the synthetic difficulties encountered in the preparation of the metal borohydride complexes. In particular, lanthanaborohydride complexes are relatively rare, and those that are known are insoluble, nonvolatile solids, rendering them inappropriate for CVD methods.[18,22] The neodymium and praseodymium borohydride complexes, in fact, are thus far entirely unknown. Thus, these metal borohydride precursors are of only very limited potential for the formation of rare earth metal boride thin films.

Recently, NdB_6 nanowires has been prepared from the reaction of BCl_3 with neodymium powder at high temperature.[23] Additionally, $Nd_3Co_{13}B_2$ films have been prepared from the flash evaporation of the pre-formed solid at high vacuum and temperature.[24] There have been no reports, however, of the chemical vapor deposition (CVD) of neodymium boride thin films in the literature.

Neodymium boride, like the hexaborides of lanthanum and gadolinium, has interesting thermionic, refractory and magnetic properties.[2] However, the neodymium and gadolinium hexaborides have not been studied in as great detail as LaB_6. In our previous investigations, we demonstrated the deposition of very high quality crystalline solid-state thin films of several metal borides by chemical vapor deposition through the vacuum copyrolysis of gas phase borane hydride clusters and metal halide vapor.[1,20,21,25] These deposition processes were found to occur at significantly lower temperatures, about 800 °C from 1600 °C, than had been previously reported for the formation of the bulk materials by traditional methodologies.[2c] Thus, we thought it to be important to investigate the CVD formation of crystalline NdB_6 thin films in our borane cluster-based deposition system.

In this paper, therefore, we report on our investigations into the formation and characterization of neodymium boride thin films using chemical vapor deposition from gas-phase rare earth metal salts and polyhedral borane clusters. We also report on the attempted synthesis of a ternary neodymium–cobalt boride thin film material.

Experimental

Physical measurements

Optical characterization

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

Structural analysis

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. 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 materials were recorded as suspensions in Nujol mulls sandwiched between NaCl plates.

Elemental composition

X-ray emission spectra (XES) were obtained on a Kevex 7500 Microanalyst System. The mass spectra were obtained on a VG 9000 glow discharge mass spectrometer using a 1 Torr argon ion discharge at 1 kV. The mass spectral analyses were performed by Shiva Technology, Inc., of Clay, New York.

Materials

The solvents used in this work were of reagent-grade or better, dried over calcium hydride, degassed by repeated freeze–evacuate–thaw cycles and finally stored *in vacuo* prior to use.[26] *Nido*-pentaborane(9), B_5H_9, was taken directly from our laboratory stock as supplied by Edwards AFB. The *nido*-decaborane(14), $B_{10}H_{14}$, was purchased from the Callery Chemical Company and was purified by vacuum sublimation at 40 °C prior to use. Appropriate care was taken in handling the boron hydrides under inert atmosphere conditions.[25,26] The anhydrous (99.9%) neodymium(III) chloride ($NdCl_3$) and cobalt(II) chloride ($CoCl_2$) were purchased form Cerac Inc. and were used as received and always handled under an inert atmosphere.

Chemical vapor deposition of neodymium boride

The thin films of neodymium boride were prepared using a medium-high vacuum hot-wall CVD pyrolytic reaction system.[25] A quartz reactor tube apparatus (1×10^{-6} Torr ultimate vacuum) was used which employed a 10 mm (o.d.) tube with an overall length of 60 cm. The portion of the reaction tube located in the furnace was approximately 40 cm in length. The apparatus was also equipped with a chromel–alumel thermocouple with the thermocouple junction located close to the tube in the middle of the oven. The reactor tube was placed horizontally in a tube furnace and heated using an external electrical resistance furnace. The overall experimental operation of the reactor employed here was similar to that described previously.[1,25]

In a typical experiment, 1.0 g (4.0 mmol) of anhydrous (99.9%) neodymium(III) chloride was placed in a quartz boat with the deposition substrates (pyrex, quartz, copper metal or ceramic) suspended directly over the top of the boat. The boat and substrates were then placed in the hot zone of the deposition system at ambient temperature using inert atmosphere techniques.[26] The entire reactor system was evacuated to 4.0×10^{-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 upstream end of 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 by adjusting the temperature of the precursor flask by using the external constant temperature bath to modify its vapor pressure.[26] The hot zone of the reactor was then slowly heated at a rate of 9 °C/min until a temperature of 835 °C (measured externally by the thermocouple) was reached under a dynamic vacuum. After a stable temperature was achieved (±5 °C), the Teflon valve to the borane reservoir flask was opened to allow a vapor of the borane to pass over the hot $NdCl_3$ while under dynamic vacuum conditions.

The unreacted borane and other reaction by-products were trapped downstream in a liquid nitrogen-cooled trap. The deposition was continued for at least 3 h, during which time a film was observed to coat both the walls of the reactor and the deposition substrates held above the $NdCl_3$ boat at a rate of 1 μm/h. The stopcock to the borane flask was closed and the reactor was allowed to cool slowly to room temperature. The reactor was then filled with dry nitrogen and the film was removed from the system for further study. The NdB_6 films thus prepared were typically navy blue in appearance.

Attempted CVD of cobalt neodymium boride films

The CVD reaction was carried out in the apparatus described above. In a typical experiment, a 1.0 g mixture of $CoCl_2$ and $NdCl_3$ (50/50 wt%) was loaded into a quartz boat which was placed in the middle of the reactor. The reactor was evacuated and heated to 700 °C. The pentaborane(9) reservoir was maintained at −78 °C and the borane was slowly introduced into the reactor. During the reaction, the temperature of the reactor was slowly raised to 850 °C over a 5 h period. This was necessary due to the different sublimation temperatures of the two metal chlorides in order to ensure the incorporation of both the metals into the film. At the end of the experiment, the reactor was cooled and the film was removed from the reactor and stored in air until further analysis.

Results and Discussion

Neodymium boride films

The pyrolytic chemical vapor deposition of pure thin films of neodymium boride was investigated through the use of volatile boron hydride cluster precursors with neodymium(III) chloride. An important goal of this work was to prepare polycrystalline NdB_6 materials at relatively low deposition temperatures (<1000 °C). If achieved, this would allow for the preparation of these thin films on relatively thermally sensitive substrates in a convenient fashion with direct applications to the formation of patterned materials. In the work reported here, we have explored the application of two readily available (commercially) boron hydride compounds, *nido*-pentaborane(9) (B_5H_9) and *nido*-decaborane(14) ($B_{10}H_{14}$), in CVD reactions. Pentaborane(9) is a highly volatile, thermally stable liquid which can be easily controlled in a flow system [vapor pressure (at 25 °C) = 209 Torr].[27a] Decaborane(14) is a less volatile, crystalline solid at room temperature [vapor pressure (at 60 °C) = 1 Torr] which still has a very suitable volatility for application in CVD processes.[27b,c] Decaborane(14), however, has the distinct advantage of being an air-stable material at room temperature while pentaborane(9) typically reacts very vigorously with the air.[28] Both of these boranes, however, gave essentially identical deposition results in the formation of the neodymium boride thin films reported here.

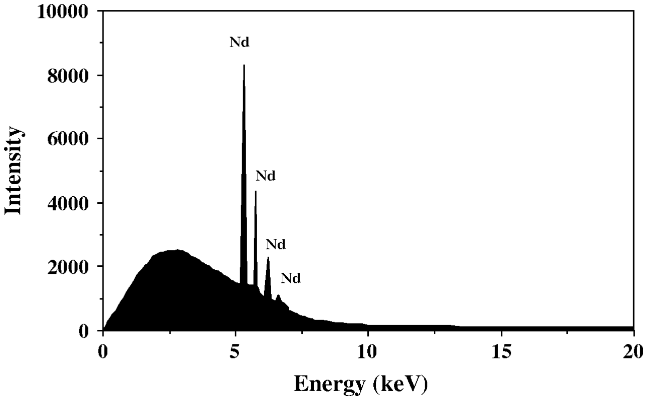

Figure 2. X-ray emission spectrum of a typical NdB_6 film. The NdB_6 polycrystalline film was deposited from neodymium(III) chloride ($NdCl_3$) and *nido*-pentaborane(9) (B_5H_9) at 850 °C on a quartz substrate (detection limits ca. 1% and boron could not be determined on the instrument).

Chemical vapor deposition experiments involving either *nido*-pentaborane(9) or *nido*-decaborane(14) with neodymium(III) chloride were found to form crystalline thin films of neodymium boride, NdB_6, on a variety of substrates which included copper, quartz, pyrex and ceramic materials. During the deposition, films of NdB_6 were observed to form in the hot zone of the reactor both on the walls of the reactor itself and on the substrates suspended horizontally in the cavity of the reactor above the $NdCl_3$ reservoir. The hot wall CVD apparatus employed in the depositions has been described in detail previously.[25] The thin films obtained were a deep blue color consistent with the reported color of large crystals of NdB_6 and adhered very well to the substrates.[29] Free-standing films could, however, be obtained, with some difficulty, by scraping the deposits from either the deposition substrates or directly from the walls of the reactor. The formation of the NdB_6 thin films was found to occur at relatively low temperatures (700–835 °C) and did not require an annealing process to obtain a crystalline material on the surface of the film as observed in the SEM. This low deposition temperature is in contrast to the reported high temperatures required for the formation of the closely related lanthanum boride materials, LaB_6, formed catalytically from a mixture of $LaCl_3$, BCl_3 and H_2 at temperatures above 1100 °C.[30]

The thicknesses of the deposited materials were readily varied by changing the flow rate of the borane precursor into the reactor (primarily by controlling the temperature of the borane reservoir by using an external cooling bath), by changing the overall time of the reaction or by changing the temperature of the deposition reactions. Thus, film thicknesses of up to several micrometers were prepared in our experiments by controlling these parameters. Typical deposition rates of 1 μm/h were observed, although higher rates were readily achieved by using higher borane flow rates. The neodymium boride films obtained from the boron hydrides were characterized by a variety of physical and chemical techniques including SEM, XRD, XES and GDMS. The results obtained from these experiments are described in detail below.

A representative X-ray emission spectrum of a typical NdB_6 film formed from $NdCl_3$ and B_5H_9 is shown in Fig. 2. In the XES analysis, strong signals due to neodymium were observed at 5.230 keV (L_α), at 5.772 keV ($L_{\beta 1}$), at 6.090 keV ($L_{\beta 2}$) and at 6.602 keV ($L_{\gamma 1}$) and is consistent with the values reported in the literature.[31] No other peaks, especially from any chlorine impurities which might be present, were detected (detection limits ca. 1% and boron could not be determined).

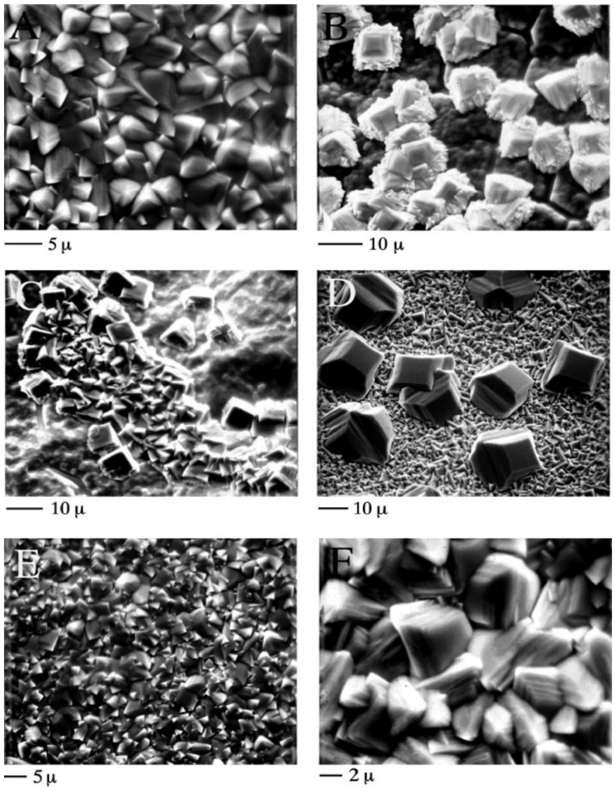

Figure 3. Scanning electron micrographs of neodymium boride (NdB_6) films deposited from neodymium(III) chloride ($NdCl_3$) and *nido*-pentaborane(9) (B_5H_9) at 850 °C on a quartz substrate. The bars below each photograph indicate scale. Micrographs (c) and (d) were annealed at 850 °C for 24 h under vacuum post-deposition. Micrographs (a), (e) and (f) were as-deposited after 3 h of precursor flow while micrograph (b) shows a film that was stopped after 1 h of flow.

Several scanning electron micrographs of typical NdB_6 films are shown in Fig. 3. All the micrographs show exceptionally well formed crystalline materials deposited on amorphous substrates. The cubic NdB_6 grains from a typical deposition were about 5 μm across. The morphology of the entire film was completely crystalline, as shown in Fig. 3. Figure 3(b) shows a deposition stopped at an early stage and incomplete coverage of the substrate. Continuing the deposition ultimately resulted in the complete coverage of the substrate by the crystalline material shown in Fig. 3(e). The cubic nature of the NdB_6 phase is evident from the micrographs, with the observed crystallites of a relatively uniform size and shape. It was also observed that the growth of the crystals was predominantly along the faces of the cubes rather than along the edges. The micrograph in Fig. 3(d) shows the growth of larger NdB_6 crystallites from a polycrystalline background. The growth appears to be in the direction of deposition and perpendicular to the substrate surface. The growth of several very large cubic crystals from the polycrystalline background is also seen in Fig. 3(d). This phenomenon is apparently similar to the growth of single crystalline NdB_6 rods from polycrystalline LaB_6.[32] The large NdB_6 cubes in Fig. 3(d) were approximately 15–20 μm across an edge.

The XRD analysis of the neodymium boride films showed sharp diffraction patterns owing to the presence of polycrystalline NdB_6 in the film. The XRD pattern is shown in Fig. 4 and the observed XRD data are compared with the reported data for NdB_6 (JCPDS file no. 3-065-5421) in Table 1. All the observed peaks were fully accounted for based upon the known data for NdB_6, with no peaks

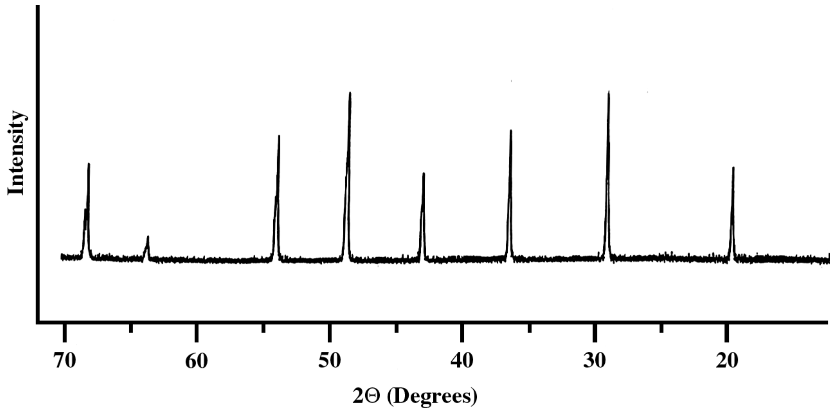

Figure 4. X-ray diffraction pattern of a typical NdB_6 polycrystalline film. The NdB_6 film was deposited from $NdCl_3$ and B_5H_9 at 850 °C on a quartz substrate.

Table 1. X-ray diffraction (XRD) data of a neodymium hexaboride film deposited from $NdCl_3$ and B_5H_9 at 850 °C on a quartz substrate as compared with reported values for NdB_6 (JCPDS file no. 3-065-5421)[a]

d spacing (Å)	*hkl*	Relative intensity observed	Relative intensity reported
4.12	*(100)*	53	55
2.91	*(110)*	100	100
2.38	*(111)*	72	45
2.06	*(200)*	54	25
1.84	*(210)*	100	55
1.68	*(211)*	62	30
1.46	*(220)*	18	13
1.38	*(300, 221)*	54	30

[a] Reflections due to NdB_6.[33]

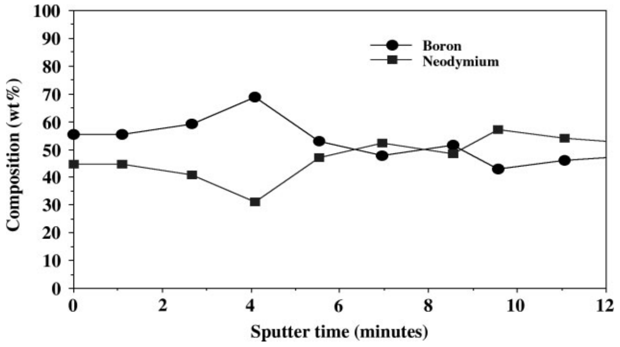

Figure 5. A plot of the NdB_6 film composition as a function of thickness. The depth profile was constructed from a series of glow discharge mass spectra recorded while the sample was being sputtered. The NdB_6 film was deposited from $NdCl_3$ and B_5H_9 at 840 °C on a ceramic substrate.

observed for crystalline elemental boron. Additionally, no peaks for the known NdB_4 phase were observed.[9b] Changes in flow rates, precursor ratios and temperature were found to yield only the NdB_6 phase.

A film deposited on a porous ceramic substrate was analyzed by glow discharge mass spectrometry to determine the atomic composition of the film. A plot of film composition as a function of sputtering time is shown in Fig. 5. The neodymium and boron concentrations were fairly uniform as a function of the depth of the film. The concentrations of boron and neodymium were fairly uniform with the average atomic composition of the film calculated from the GDMS data to be $NdB_{8.9,}$ indicating that the film contained NdB_6 and some free boron. Free elemental contamination, such as carbon, oxygen, nitrogen and chlorine, was not found. The surface layers also were found to contain a higher concentration of boron compared with the bulk of the film. The presence of elemental boron in the films would be anticipated since in our apparatus the borane precursor is always in large excess relative to the metal in the gas phase. The lower neodymium content at the surface of the film is most likely due to a depletion of the neodymium(III) chloride from the source reservoir boat and also, therefore, from the gas phase as the reaction proceeds.[1]

A possible explanation for this is that the surface of the neodymium(III) chloride reservoir becomes contaminated with a refractory layer of either neodymium boride or native boron. As this source reservoir coverage occurs, the relative neodymium concentration in the gas phase decreases. This surface contamination has been observed previously for transition metal borides in the higher temperature ranges as a black layer coating the surface of the reservoir.[1,25] Since the gas-phase boron concentration is essentially constant throughout the deposition experiment, a relative depletion of the gas-phase neodymium content as the experiment progresses would be anticipated. A very small amount of chlorine impurity incorporation, as noted in the other hexaborides deposited on porous ceramic substrates, was also observed in the NdB_6 film as analyzed by mass spectrometry.[1] Previous mass spectral studies of $NdCl_3$ in the literature above 782 °C have shown that dissociation of the trihalide into $NdCl_2$, NdCl and Nd takes place and the relative intensities of these species were 100, 18.4 and 16%, respectively (along with Cl_2 and HCl).[34] The porous microstructure of the substrate can easily trap such reactive species. The observation of chlorine diffusion into a pure nickel surface from $NiCl_2$ overlayers has also been reported earlier.[31] Thus, the diffusion of such metal subhalide species into the deposited film cannot be ruled out. These species may also react chemically either with the substrate or the deposited film. These observations support the possibility of a very small amount of chlorine diffusion and incorporation into the film from the trapped metal halide species into the porous substrate.

Attempted formation of transition metal–neodymium–boride films

Transition metal-rare earth metal–boron ternary alloys are widely used as very strong permanent magnets. Both cobalt samar-

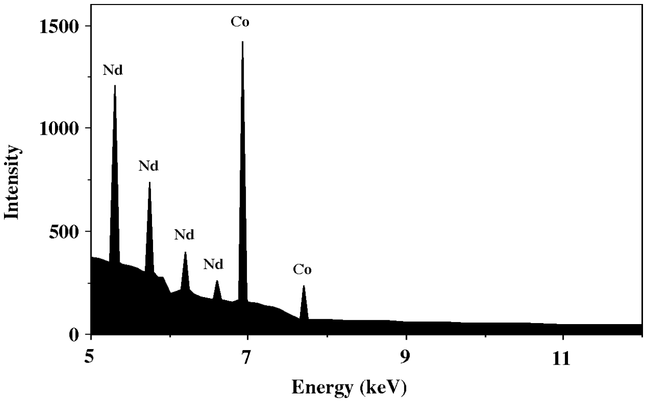

Figure 6. X-ray emission spectrum of a Co–Nd–B film. The film was found to consist of cobalt boride (CoB) and neodymium boride (NdB_6) phases. The film was deposited from $CoCl_2$, $NdCl_3$ and B_5H_9 on a quartz substrate. The temperature of the CVD reaction was slowly raised from 700 to 850 °C over a 5 h period.

ium boride, with at least nine ternary alloys known, and iron neodymium boride ($Nd_2Fe_{14}B$) have found widespread application as permanent magnets.[35] Considering the technological importance of these ternary alloys, we attempted to synthesize a mixed metal cobalt–neodymium ternary phase thin film. Cobalt and neodymium were also chosen for this investigation since both the metals form alloys with useful magnetic properties and have well-characterized known boride phases.

The formation of Co–Nd–B films was attempted by pyrolytic co-deposition using $CoCl_2$, $NdCl_3$ and B_5H_9 as the CVD precursors in the apparatus previously described. The deposited films were blue and adhered well to the substrates. The analysis of the films was performed using SEM, XES and XRD techniques (*vide infra*).

The X-ray emission spectrum, shown in Fig. 6, of a film formed from the pyrolytic deposition of $CoCl_2$, $NdCl_3$ and B_5H_9 showed intense signals due to cobalt at 6.925 keV (K_α) and at 7.649 keV ($K_ß$), while signals due to neodymium were detected at 5.230 keV (L_α), at 5.772 keV ($L_{ß1}$), at 6.090 keV ($L_{ß2}$) and at 6.602 keV ($L_{\gamma 1}$) consistent with those reported in literature.[31] No chlorine was detected in the film. When the depositions were performed at lower temperatures (between 700 and 800 °C), no neodymium was found in the films with only Co/Co_3B, Co/Co_2B and CoB deposited materials, as determined by X-ray powder diffraction. By raising the temperature, however, it was possible to incorporate neodymium into the films. If the CVD was started at 800 °C or above, no cobalt was found in the films and only NdB_6 films were obtained. Instead of the simultaneous deposition of both metals, we were able to deposit only a mixture of two binary metal boride phases.

The XRD pattern for the film deposited from $CoCl_2$, $NdCl_3$ and B_5H_9 is shown in Fig. 7 and the observed data are compared with the known XRD data for cobalt (JCPDS file no. 3-0959) and neodymium boride (JCPDS file no. 3-065-5421) in Table 2. The XRD confirmed that the film consisted of a mixture of NdB_6 and CoB

Table 2. X-ray diffraction data of a cobalt-neodymium boride film containing cobalt boride (JCPDS file no. 3-0959) and neodymium hexaboride (JCPDS file no. 3-065-5421)[a]

d spacing (Å)	*hkl*	Relative intensity observed[b]	Relative intensity reported	Identity[c]
4.12	*(100)*	51	55	NdB_6
2.91	*(110)*	100	100	NdB_6
2.41	*(101)*	31 (84)	100	CoB
2.38	*(111)*	65	45	NdB_6
2.19	*(111)*	37 (100)	100	CoB
2.06	*(200)*	46	25	NdB_6
1.98	*(021)*	34 (91)	80	CoB
1.84	*(210)*	85	55	NdB_6
1.78	*(121)*	24 (64)	60	CoB
1.68	*(211)*	43	30	NdB_6
1.60	*(130)*	22 (60)	60	CoB
1.58	*(211)*	22 (60)	60	CoB
1.52	*(002)*	22 (60)	60	CoB
1.46	*(220)*	29	13	NdB_6
1.37	*(300), (221)*	50	30	NdB_6

[a] The film was deposited from $CoCl_2$, $NdCl_3$ and B_5H_9 on a quartz substrate. The temperature of the CVD reaction was slowly raised from 700 to 850 °C over a 5 h period. [b] Values in parentheses correspond to normalized CoB XRD observed peak intensities. [c] Reflections due to NdB_6,[33] and reflections due to CoB.[36]

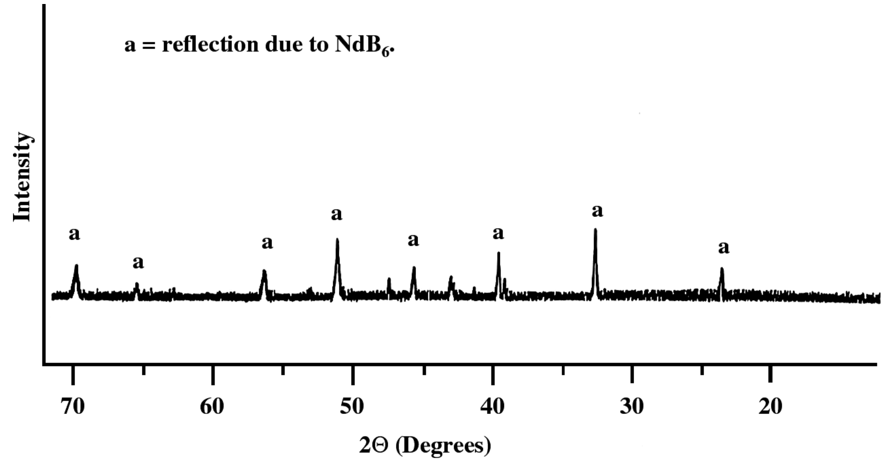

Figure 7. X-ray diffraction pattern of a cobalt–neodymium boride film. The film was found to consist of cobalt boride (CoB) (JCPDS file no. 3-0959) and neodymium boride (NdB_6) (JCPDS file no. 3-065-5421). The film was deposited from $CoCl_2$, $NdCl_3$ and B_5H_9 on a quartz substrate. The temperature of the CVD reaction was slowly raised from 700 °C to 850 °C over a 5 h period. The reflections labeled ‘a’ belong to NdB_6 while other reflections are due to CoB.

with a ratio of 3.6 to 1. Because of the arrangement of our reaction system, it was not possible to differentially heat the two metal sources separately.

Conclusions

Polycrystalline NdB_6 films can be readily prepared from the CVD of neodymium(III) chloride and borane clusters, such as *nido*-pentaborane(9) and *nido*-decaborane(14). The neodymium boride films were found to contain very little, if any, contamination. Deposition experiments on the formation of Co–Nd–B ternary phase films using $CoCl_2$, $NdCl_3$ and B_5H_9 as the CVD precursors resulted only, however, in the formation of a mixture of discrete NdB_6 or CoB phases rather that the ternary phase.

These experiments indicate that the CVD formation of solid state borides from metal halides and borane cluster precursors provides a general and versatile route to crystalline metal boride thin films such as neodymium boride.

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