

CHEMICAL VAPOR DEPOSITION OF METAL BORIDES 7. THE RELATIVELY LOW TEMPERATURE FORMATION OF CRYSTALLINE LANTHANUM HEXABORIDE THIN FILMS FROM BORON HYDRIDE CLUSTER COMPOUNDS BY CHEMICAL VAPOR DEPOSITION[1]

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Abstract—The chemical vapor deposition (CVD) of high quality polycrystalline thin films of lanthanum hexaboride, LaB₆, was achieved through the vacuum copyrolysis of the boron hydride clusters, *nido*-pentaborane(9) [B₅H₉] and *nido*-decaborane(14) [B₁₀H₁₄], with lanthanum(III) chloride at 800–900°C. The reddish purple films adhered well to the deposition substrates explored (copper, quartz, Pyrex and ceramic materials). Deposition rates of approximately $1-2 \mu m/h$ were typically observed. The films were analyzed by scanning electron microscopy (SEM), X-ray emission spectroscopy (XES), X-ray diffraction (XRD), wavelength dispersive X-ray emission spectrometry (WDXES), and glow discharge mass spectrometry (GDMS). WDXES and GDMS data showed that the LaB₆ films were relatively uniform in composition in the bulk material. SEM data showed that the as-deposited materials were very highly crystalline. Films which consisted either partly or entirely of square rods of LaB₆ with either square or finely tapered tips could also be grown. Reflection high energy electron diffraction (RHEED) experiments confirmed the identity of the square rods as crystalline cubic LaB₆. © 1998 Elsevier Science Ltd. All rights reserved

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1. BACKGROUND

The theoretical features [1, 2], synthesis [3, 4], and solid state characteristics[5] of the transition and lanthanide metal boride materials[1] have received significant recent interest primarily due to the magnetic, electrical and catalytic[6] properties of these materials. Metal borides typically display a unique range of structural types not seen in other solid state materials with many discrete metal-to-boron ratios and solid state structures frequently observed for a given metal[3, 4]. The boron atoms in these materials display a very strong tendency to form bonds with each other throughout the crystal, leading to a variety of rather complex solid state structures. These structures vary from the metal rich borides, which contain isolated boron atoms within a metal lattice, such as in Mn₄B and Co₃B, to the boron-rich materials with threedimensional networks of linked boron octahedra and icosahedra, such as in LaB₆ and YB₁₂ [3, 4]. The metal borides are also extremely refractory and exceptionally hard materials which are resistant to chemical attack even in the most harsh of environments, including prolonged treatment with concentrated mineral acid[5]. Although

nitride is an insulator, the metal borides are typically excellent metallic conductors, with conductivities usually significantly higher than those observed for the pure metals[4], with some borides even becoming superconducting at low temperatures (i.e. T_c of 8.25 K for NbB)[7]. Work done with single crystalline metal borides, in which the crystalline voids have been essentially eliminated, shows that the ultimate resistivities of these materials approaches those of the very best metallic conductors (i.e. 1.1 and 2.9 mohm cm for TiB_2 and ZrB_2 , respectively)[8]. Metal boride materials, such as HfB₂, are currently used as electrodes and photothermal absorbers, which capitalize on these physical and electronic properties[9]. In addition, metal borides have found use in a wide range of applications including in thermally and chemically taxed aerospace components[10], in high-energy optical systems[11], as magnetic materials[12], as electrical coatings for resistors, and as thermionic materials[13].

elemental boron is a semiconductor and pure boron

Rare earth metal borides are of special interest, due to their physical, magnetic and electrical properties. The lanthanide elements, unlike the transition metals, tend to form boron-rich materials rather than the metal-rich phases. These rare earth hexaboride structures consist

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of frameworks of boron octahedra arranged as units in a body centered cubic lattice[14]. The covalent bonding within the boron polyhedra is believed to impart great stability, hardness and high melting points to these borides.

The thermionic emissive properties of the rare earth hexaborides have been studied in detail, and these materials have been found to possess very low work functions which are, in fact, lower than for any other known materials (i.e. work functions of 2.74 and 2.22 eV for LaB₆ and YB₆, respectively)[15, 16]. Of all the rare earth borides, lanthanum hexaboride is of particular interest due to its use as an electron emissive (thermionic) material[15, 16]. Lanthanum hexaboride has the highest electronic emissivity of any known material and its performance is unaffected by the presence of either nitrogen or oxygen[17]. Lanthanum hexaboride thin film cathodes have recently been successfully used to replace nickel cathodes in display panels. These rare earth boride cathodes have been shown to work very efficiently at significantly lower voltages than the corresponding nickel cathodes. The sputtering rates of the LaB₆ thin films in these cathodes were also found to be only about one third the rate of sputtering of the traditional nickel cathodes[18].

A variety of metal borides have been prepared in bulk either by reacting the desired pure metal with elemental boron at high temperatures, typically above 1000°C, or by reacting metal oxides with boron carbide, again at high temperatures, to yield the metal borides and carbon monoxide[19]. Metal boride coatings have in the past been primarily prepared by the electrolytic deposition of the materials either from fused molten salts[3, 4] or from solution[20]. Due to the great temperatures required and/ or the nature of the metal boride products themselves, pure metal boride materials have been particularly difficult to prepare in these fashions.

There are several reports on the preparation of lanthanum hexaboride thin films. These films have been prepared by sputtering[21], evaporation[18], vapor transport[22] and chemical vapor deposition (CVD) processes[23, 24]. Lanthanum hexaboride crystals have been grown from the reaction of a $La/Cl_2/BCl_3/H_2/Ar$ mixture at 1000–1350°C. In this CVD method, $LaCl_3$ was generated *in situ* from the thermal reaction of chlorine with lanthanum metal while BCl₃ was generated *in situ* by passing Cl₂ through boron carbide at 800°C. The deposition of lanthanum hexaboride films has also been reported from $LaCl_3/BCl_3/H_2/HCl$ mixtures at 900–1500°C[23, 24].

CVD methodologies have been shown to be among the most effective current techniques for the formation of clean thin film materials[25, 26]. In recognition of the advantages offered by CVD reaction systems, considerable effort has been directed toward employing CVD techniques for the preparation of refractory thin films[27]. One approach in the CVD formation of metal borides has been through the use of metallaborane precursors. Iron boride films have recently been reported from the thermolysis of various metallaborane precursors such as $HFe_3(CO)_9BH_4$ [28], $HFe_3(CO)_{10}BH_2$ [29], $[B_2H_4Fe_2(CO)_6]_2$ and $B_2H_6Fe_2(CO)_6$ [30] at 200-300°C[28-30]. Also, the formation of titanium diboride by CVD has been achieved from a titanium borohydride compound, but the as-deposited films were amorphous and pyrophoric volatile borane by-products were reported to be formed from these precursors[31]. In general, metallaborane compounds, however, are airsensitive (even pyrophoric for many borohydride compounds) and usually involve very difficult syntheses with low yields of the desired products. In addition to these problems, some metallaborane compounds have been shown to deposit metal borides only above 1000°C[32].

An ideal choice for metal boride thin film formation by CVD would employ very inexpensive and abundant starting materials, such as metal halides and boranes as CVD precursors, and be generally applicable to a wide variety of metal systems. Once such a procedure is established, it might be possible to employ essentially any metal halide to deposit the desired boride films with only minor adjustments of the deposition parameters. In this paper, we report on our continuing investigations into the preparation of metal boride thin films using chemical vapor deposition from metal halides and polyhedral borane clusters. Specifically, we report here on the preparation of crystalline, high purity thin films of lanthanum hexaboride from lanthanum(III) chloride with either *nido*-pentaborane(9) or *nido*-decaborane(14).

2. EXPERIMENTAL

2.1. Physical measurements

Fourier transform infra-red (FT-IR) spectra in the range of 400 to 4000 cm⁻¹ were measured on a Mattson Galaxy 2020 spectrometer and were referenced to the 1601.8 cm⁻¹ band of polystyrene. Scanning electron micrographs (SEM) were obtained on an ETEC autoscan instrument in the N.C. Brown Center for Ultrastructure Studies of the S.U.N.Y. College of Environmental Science and Forestry. Photographs were recorded on either Kodak Ektapan 4162 or Polaroid P/N 55 film. Xray 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. $Cu-K_{\alpha}$ radiation and a graphite single crystal monochromator were employed in the measurements reported here. The Auger electron spectra (AES) were measured on either a Perkin Elmer PHI 595 scanning Auger microprobe instrument in the Electronics Laboratory of Lockheed-Martin, Syracuse, New York or a similar instrument at the U.S.A.F. Rome Laboratory, Rome, New York. Depth profiles were obtained by alternately sputtering the top of the sample with an Ar⁺ ion beam and measuring the AES spectrum. The profiles were obtained using a 10 kV, 150 nA rastered electron beam and an argon ion beam at 3.5 kV and 860 nA/mm². The relative concentrations for all elements except hydrogen and helium were measured in the spectra. The mass spectra were obtained on a VG 9000 glow discharge mass spectrometer (GDMS) using a 1 torr argon discharge at 1 kV. Depth profiles were obtained by alternately sputtering the top of the sample with an Ar⁺ ion beam and measuring the GDMS spectrum. The mass spectral analyses were performed at Shiva Technology, Inc., Clay, NY.

2.2. Materials

The *nido*-pentaborane(9), B_5H_9 , was from our laboratory stock as supplied by Edwards AFB. *Nido*-decaborane(14), $B_{10}H_{14}$, was purchased from Callery Chemical Company and was purified by sublimation before use. Anhydrous (99%) lanthanum(III) chloride was purchased from Cerac, Inc. and used as received without further purification.

2.3. Formation of lanthanum hexaboride films

The experimental medium-high vacuum, hot-wall CVD pyrolytic reaction apparatus used for depositing the LaB₆ films has been described in detail previously[1]. In a typical experiment, 1.0 g (4.1 mmol) of LaCl₃ was placed in a quartz boat and the substrate (Pyrex, quartz, copper metal or ceramic) was placed directly over the boat. After placing the boat in the reactor, the system was evacuated to 4×10^{-6} mm and heated to 815° C under dynamic vacuum. A boron precursor reservoir containing either freshly sublimed nido-decaborane(14), B₁₀H₁₄, or vacuum distilled nido-pentaborane(9), B5H9, was connected to the downstream 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 through the use of narrow bore Teflon vacuum stopcocks (0-4 mm) and by adjusting the temperature of the precursor flask by using the external constant temperature bath to modify its vapor pressure. The deposition was continued for 4 h, during which time a film was observed to coat both the walls of the reactor and the deposition substrates held above the LaCl₃ boat. The stopcock to the borane flask was closed and the reactor was allowed to cool slowly to room temperature. The cooled reactor was filled with nitrogen and the films

were removed for further analysis. The films thus deposited were reddish purple materials.

In the CVD reactions, HCl was expected to be formed as a by-product from the reaction of $LaCl_3$ with the borane cluster. In order to gain some information concerning HCl generation, a piece of blue litmus paper was placed in the liquid nitrogen cooled trap prior to cooling the trap for one of the LaB_6 CVD experiments. The reactor and the trap were evacuated and the reaction by-products were condensed into the trap. At the end of the experiment, the Teflon valves on the trap were closed and the trap was slowly warmed to room temperature. The blue litmus paper turned red indicating presence of an acidic species, possibly HCl.

3. RESULTS AND DISCUSSION

In our work, LaB₆ films were prepared from pyrolytic CVD methods using lanthanum(III) chloride with either of two readily available boranes, nido-pentaborane(9) (B_5H_9) or *nido*-decaborane(14) $(B_{10}H_{14})$. Both of these boranes gave very similar deposition results in the formation of the lanthanum boride thin films reported here. Nido-pentaborane(9) was used preferentially, however, since it is a very volatile liquid which can be easily controlled in a flow system. The deposited LaB₆ films were reddish purple and adhered well to the deposition substrates, which included copper, quartz, Pyrex and ceramic materials. The preparation of these lanthanum hexaboride films occurred at significantly lower temperatures (815°C) than previously reported preparations and did not require any annealing in order to obtain very well formed crystalline materials (vide infra). The low deposition temperature observed here is in strong contrast to the previously reported high temperatures required for the formation of lanthanum boride materials which were formed catalytically from a mixture of LaCl₃, BCl₃ and H₂ at temperatures above 1100°C[23, 24]. As in our previous work, the thicknesses of the solid state materials (up to several micrometers) were readily varied by changing the flow rate of the borane precursor into the reactor, by changing the overall time of the reaction or by changing the temperature of the deposition reaction. Deposition rates of approximately $1-2 \mu m/h$ were typically observed. The films from the boron hydrides were analyzed by a variety of techniques including SEM, XRD, XES, and GDMS.

An XES of a typical LaB₆ film prepared from LaCl₃ and *nido*-pentaborane(9) at 815°C is shown in Fig. 1. The XES analysis showed strong lanthanum signals at 4.651 keV (L_{α}), 5.043 keV ($L_{\beta1}$), 5.384 keV ($L_{\beta2}$) and 5.789 keV ($L_{\gamma1}$). No impurities, such as chlorine, were detected in the spectra (boron could not be detected in our XES analysis). SEMs of several typical LaB₆ deposited films are shown in Fig. 2. Very similar results were



Fig. 1. XES of a typical LaB₆ film. The film was deposited from LaCl₃ and B₅H₉ at 815°C on a quartz substrate.

obtained when the nido-pentaborane(9) was replaced with nido-decaborane(14) as the borane precursor. All the films appeared to be polycrystalline and consisted of cubic grains, typically about $1-2 \mu m$ in size. Polycrystalline LaB₆ films are highly desirable for a wide variety of potential materials applications, especially as photoemissive materials[23, 24]. The films were found to be conformal and did not show significant void formation. The absence of voids in the these films formed at the relatively low temperatures employed here is somewhat surprising, however, since this deposition temperature is significantly below the melting point of either the pure material or the metal boride phase[3, 4]. 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 problems associated with insufficient surface mobility effects[33].

The XRD analysis of the film shown in Fig. 2(a) confirmed that the film consisted of crystalline, cubic LaB₆. The XRD pattern for this film is shown in Fig. 3 and the observed data are compared with the reported XRD data for LaB₆ in Table 1.

In some regions of the deposited film, scanning electron micrographs showed square rods growing out of the polycrystalline background (Fig. 2(b)–(e)). The rods were typically found to be approximately 5–10 μ m in length and about 0.5 μ m across. The thickness of the square rods precluded their identification by transmission electron diffraction. In order to confirm the identity of the rods, however, another LaB₆ film was deposited at 895°C

on a ceramic substrate. A SEM examination of this film grown on the ceramic substrate, displayed in Fig. 2(f) and Fig. 4(a), showed that it consisted entirely of the well formed square rods. These rods, however, had roughly twice the thickness (about $1 \mu m$) of the previously prepared rods (Fig. 2(b)). The length of the rods were also significantly longer and averaged approximately 10-15 μ m in length. In addition, the tips of these rods were not square but rather were tapered to very sharp points. The fineness of the tips could not be accurately resolved by scanning electron microscopy but were estimated to be less than 0.1 μ m across the tip. A tapered crystalline morphology such as observed here may be particularly useful in the thermionic applications of LaB₆ crystals. In applications such as electron microscopy and electron beam lithography, fine crystallite tips are required since this morphology allows the best generation of finely focused electron beams. Current practice requires the rather laborious sharpening of individual LaB₆ crystals for these applications[22]. The formation of LaB₆ materials with such tapers has only been observed previously either using LaCl₃/BCl₃/H₂ mixtures at very high temperatures (i.e. 1250°C)[22] or when the films were grown under very high reactor pressures[23]. Even under these rather extreme conditions, the tips of the crystals that were generated were not as fine as those obtained for the films shown in Fig. 4(a).

The identification of the square rods as cubic LaB_6 was confirmed by reflection high energy electron diffraction (RHEED) experiments. The RHEED pattern from a LaB_6 film consisting entirely of the cubic rods is shown, along



Fig. 2. SEMs of lanthanum hexaboride (LaB₆) films. The bars in each photograph indicate the scale. Micrographs (a)–(e) were deposited from LaCl₃ and B₅H₉ at 815°C on a quartz substrate. Micrograph (f) was deposited from LaCl₃ and B₅H₉ at 895°C on a ceramic substrate.



Fig. 3. XRD pattern of a typical LaB_6 film. The film was deposited from $LaCl_3$ and B_5H_9 at 815°C on a quartz substrate.

d spacing (Å)	hkl	Relative intensity observed	Relative intensity reported	
4.15	(100)	0	54	
2.94	(110)	62	100	
2.40	(111)	100	41	
2.08	(200)	0	22	
1.86	(210)	20	46	
1.70	(211)	37	24	
1.47	(220)	13	8	
1.39	(300)	45	23	

Table 1. Observed and Literature XRD Data for Lanthanum Hexaboride^{a,b}

^aReflections due to LaB_{6} [34].

^bThe LaB₆ film was deposited from LaCl₃ and B₅H₉ at 815°C on a quartz substrate.

with its corresponding SEM, in Fig. 4. In order to obtain meaningful results from the RHEED experiment, it was essential that the film consisted entirely of the square rods and that no polycrystalline background be present. If LaB₆ from the background were present, any observed LaB₆ diffraction pattern from the background would be indistinguishable from pattern obtained from the square rods. The RHEED experiment performed solely on the cubic rods in Fig. 4(a) gave the diffraction pattern shown in Fig. 4(b). The observed pattern matched very well with the reported XRD data for cubic LaB₆ [34]. The results of our RHEED experiment confirmed the identity of the square rods as crystalline cubic LaB₆.

A LaB₆ film deposited at 815°C on a quartz substrate was analyzed by wavelength dispersive X-ray emission spectrometry (WDXES). This technique gives high resolution spectra and is much more sensitive than the XES analysis. The wavelength dispersive technique detects wavelengths of the characteristic X-rays emitted by the elements in the sample and detects as little as 0.1 wt% of an element above atomic number 2. A quantitative elemental analysis of material is also possible using this technique. A typical LaB₆ film deposited for 4 h was analyzed by WDXES and found to be approximately $6.2 \,\mu m$ thick, giving a rate of deposition of about approximately $1.6 \,\mu\text{m/h}$. The surface of the film was found to contain 69.5 wt% boron and 30.5 wt% lanthanum with the bulk composition of the film at 64 wt% lanthanum and 36 wt% boron. This analysis indicates that the film was composed of primarily LaB₆ and with some elemental boron. The film was also found to contain only trace amounts of chlorine (0.1-0.2 wt%), presumably from the contamination of the film at the end of the deposition process. The composition of the film was found to be uniform in the bulk sample.

A film deposited at 865°C for 2 h on a porous ceramic substrate was also analyzed by GDMS. This film was deposited under lower initial reactor pressure conditions $(5 \times 10^{-5} \text{ mm})$ than the film analyzed by WDXES (4 \times 10^{-4} mm). In the GDMS analysis of this sample, it was found that more boron was incorporated into the upper layers of the film compared with the WDXES analyzed film. A profile of the film composition as a function of the depth, shown in Fig. 5, was plotted from a series of glow discharge mass spectra. The surface of the film was composed of 40 wt% lanthanum and 60 wt% boron. The film composition remained relatively constant for a depth of a few microns then gradually the boron concentration was found to increase. The bulk composition of the film was determined to be LaB_{8.6}, which again indicated that the film consisted of LaB₆ and some free boron. The boron-rich films are typically bluish purple while the lanthanum-rich films are usually reddish purple[22]. The lower lanthanum concentration in the GDMS analyzed film is presumably due to a higher gas phase boron concentration from a greater borane precursor flow. In experiments carried out at 4×10^{-4} mm initial reactor pressure, such as for the WDXES analyzed sample, the amount of pentaborane(9) consumed was typically 50-60 mg in a 4 h experiment, and in the GDMS analyzed film almost twice this amount of borane source was consumed in half the deposition



Fig. 4. SEM and RHEED data of a typical LaB₆ film. (a) SEM of a LaB₆ film deposited from LaCl₃ and B₅H₉ at 895°C on a ceramic substrate. The film was observed to consist entirely of tapered square rods. The bar in the lower left corner indicates the scale. (b) RHEED pattern obtained from the LaB₆ film shown in (a).



Fig. 5. A plot of the LaB $_6$ film composition as a function of sputtering time (thickness). The depth profile was constructed from a series of glow discharge mass spectra recorded while the sample was being Ar + sputtered. The film was deposited from LaCl₃ and B₅H₉ at 870°C on a ceramic substrate.

time. In our experimental setup, the borane flow is controlled primarily by modifying the temperature of the borane reservoir and by varying the opening of the Teflon valve to the borane reservoir. Both of these control mechanisms are relatively difficult to regulate accurately, thus leading to a higher boron content in the WDXES analyzed film. The slightly higher chlorine content of the film deposited on the porous ceramic substrate compared with the film deposited on the quartz substrate probably arises from the porous nature of the ceramic substrate which can easily trap some metal halide within the substrate and also, therefore, within the forming film. This leads to the formation of LaCl_x inclusions in the growing film. Since the quartz substrate used in the film deposited at 815°C provides a relatively non-porous surface, negligible amounts of chlorine (0.1-0.2 wt%) from this inclusion mechanism were incorporated into the film. It is also possible that, since the films were deposited at slightly different temperatures (815 and 870°C), a different mixture of gas phase lanthanum reactive species leads to a slightly different CVD reaction profile. The dissociation of LaCl₃ into lanthanum subhalides is known to occur above 757°C[35], and a mass spectral study has indicated that $LaCl_2 + (100\%)$, $LaCl^+$ and $La^+ (0.2\% each)$ are formed in this pyrolysis[35]. The relative abundance of these species is temperature dependent. It is thus possible that the lower halide species, LaCl₂ and LaCl, may have somewhat different relative reaction rates with the borane precursor which, in turn, leads to different deposition rates

and profiles. Although, this mechanism may play a role in incorporating 0.1-0.2 wt% chlorine in the film deposited on quartz, it appears that the porous nature of the ceramic substrate may still be most important in the entrapment and the inclusion of chlorine in the depositing film on ceramics.

The pyrolysis of boranes at 50-250°C has been studied in a great detail[36]. Although many groups have investigated the pyrolysis of boranes, a very few reports of pyrolysis of pentaborane(9)[37] and decaborane(14)[38] exist. During pyrolysis, boranes are known to rapidly convert to other boranes with the generation of hydrogen[36-38]. In addition, non-volatile and air-sensitive solid BH_x polymers are formed[36–38]. It is possible that in our CVD reactions, such polymeric solids may play an important role in the formation of the metal boride films. These polymeric solids are known to consist of frameworks and networks of B-B covalent bonds. These frameworks are closely related structurally to those found in the crystalline metal boride phases. Since all of our low temperature as-deposited films are crystalline, it is possible that the existing boron frameworks and networks formed in the pyrolysis of the borane precursors facilitate the CVD of polycrystalline metal borides.

4. CONCLUSION

The results of our investigation of the CVD of LaB_6 films indicate that the use of lanthanum(III) chloride with borane clusters gives highly crystalline LaB_6 films at much lower deposition temperatures than previously observed. The morphology of the crystallites obtained in these LaB₆ films shows the selective formation of conformal polycrystalline films, cubic rods or tapered cubic rods, depending upon the deposition conditions employed. Although no data is available to compare the film compositions obtained in our experiments with those from the previously reported LaCl₃/BCl₃/H₂ system, the results of our analysis indicate that without optimization of our experimental parameters, we have been able to deposit compositionally uniform, excellent quality LaB₆ films with negligible amounts of contamination (0.1-0.2 wt%).

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