Chemical Vapor Deposition Precursor Chemistry. 2. Formation of Pure Aluminum, Alumina, and Aluminum Boride Thin Films from Boron-Containing Precursor Compounds by Chemical Vapor Deposition[1]

John A. Glass Jr., Shreyas S. Kher, and James T. Spencer*

Department of Chemistry and Center for Molecular Electronics, Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100

Received June 28, 1991. Revised Manuscript Received January 31, 1992

Thin films of pure aluminum, aluminum boride, and aluminum oxide have been prepared from the chemical vapor deposition (CVD) of volatile boron-containing precursor compounds. Chemical vapor depositions on a variety of amorphous and monolithic substrates have been explored for the source compounds $Al(BH_4)_3$, 1, and $AlH_2(BH_4){\cdot}N(CH_3)_3$, 2. The formation of pure polycrystalline aluminum thin films from 2 was accomplished at 100 °C without substrate pretreatment, and at 25 °C with the substrate briefly pretreated with $TiCl_4$. Room-temperature depositions of mirrorlike pure polycrystalline aluminum films were demonstrated on thermally sensitive substrates. Aluminum boride films were similarly prepared from compound 1 at >300 °C. Depositions with 1 in a partial pressure of oxygen yielded pure polycrystalline alumina (Al_2O_3) films. All films were characterized by XES, AES, SEM, XRD, and resistivity measurements. Each film was shown by AES to be compositionally uniform in the bulk sample with only very shallow surface contaminations of oxygen and carbon from atmospheric exposure. Film thicknesses ranging from 500 Å to 2 μm were readily prepared by controlling the precursor flow rate into the cell, the substrate temperature, the precursor exposure times to the substrate, and the nature of the substrate pretreatment. The two source compounds were, in general, relatively thermally stable, volatile, air-sensitive liquids, thus providing excellent precursor properties for chemical vapor deposition experiments.

Introduction

The formation of thin film materials which incorporate main group elements into the epitaxial layer, such as GaAs and $Al_xGa_{1-x}As$, using metalloorganic source compounds has received a great deal of attention.[2] The use of $Al_xGa_{1-x}As$ and related materials in high-performance applications, such as high-frequency communication systems using high electron mobility transistors (HEMT), heterojunction bipolar transistors (HBT), ultra-high-speed systems, optoelectronic devices, and others, presents challenging materials requirements. Producing these high-performance materials will require the optimization of the chemical and materials technology used to synthesize these epitaxial structures. Few existing epitaxial growth technologies can meet these demanding requirements. For example, older epi-growth techniques, such as liquid-phase epitaxy (LPE) and vapor-phase epitaxy (VPE), operate close to thermodynamic equilibrium.[2] Consequently, growth rate and composition are highly temperature sensitive. In addition, heterostructures with sharp interfaces are very difficult to prepare using these older technologies. Metalloorganic chemical vapor deposition (MOCVD) and metalloorganic molecular beam epitaxy (MOMBE),[2] which are kinetically controlled, show great promise as the best technologies for the formation of these materials since they circumvent many of the problems associated with other deposition technologies. Thus, the realization of the incorporation of new materials into these demanding applications may best be achieved through the use of chemical vapor deposition (CVD) technology which provides advantages over traditional deposition methods, including (1) kinetic deposition control, (2) selective area and pattern deposition capabilities, (3) lower deposition temperatures, (4) superior step coverage and via filling, (5) monolayer interfacial control and (6) the formation of high-purity materials.[2]

Research in chemical vapor deposition has focused primarily on the development of new epitaxial techniques and the purification of existent main group and organometallic source materials. There are, however, a number of important problems associated with the epitaxial source materials currently in use. These problems include (1) severe substrate reactivity and bonding problems, (2) high toxicity (and the related environmental and occupational concerns), (3) great difficulties in handling and manipulation, and (4) the undesired co-deposition of carbon and other contaminant elements. In many cases, the most difficult problem is that the films derived from organometallic precursor compounds contain unacceptably high carbon levels, thus effectively limiting the material properties of the films. While these source compounds have proven adequate in many instances, further developments and improvements in epitaxial processes must now rely upon the cognizant and systematic design and synthesis of new source materials developed to exhibit enhanced chemical properties for depositional processes. Thus far, relatively little emphasis has been placed on this vitally important aspect of epitaxial science.

The formation of pure aluminum and aluminum-containing alloy thin films has typically been among the most troublesome materials.[2,3] Many of the currently employed aluminum precursor compounds are prone to contamination and reactivity problems. With the emergence of ternary structures, such as $Al_xGa_{1-x}As$, as vital electronic materials, and the recent demand for pure aluminum and related materials (such as alumina and aluminum boride),[3]

---

[1] Part 1: Glass, J. A., Jr.; Kher, S.; Spencer, J. T. *Thin Solid Films* **1992**, *207*, 15.

[2] (a) Leys, M. R. *Chemtronics* **1987**, *2*, 155. (b) Davies, G. J.; Andrews, D. A. *Chemtronics* **1988**, *3*, 3. (c) Jones, A. C.; Roberts, J. S.; Wright, P. J.; Oliver, P. E.; Cockayne, B. *Chemtronics* **1988**, *3*, 152.

[3] (a) Pande, K. P.; Nair, V. K. R.; Gutierrez, D. *J. Appl. Phys.* **1983**, *54*, 5436. (b) Saraie, J.; Kwon, J.; Yodogawa, Y. *J. Electrochem. Soc.* **1985**, *132*, 890. (c) Saraie, J.; Ono, K.; Takeuchi, S. *J. Electrochem. Soc.* **1989**, *136*, 3139. (d) Fournier, J.; DeSisto, W.; Brusasco, R.; Sosnowski, M.; Kershaw, R.; Baglio, J.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1988**, *23*, 31. (e) Dhanavantri, C.; Karekar, R. N.; Rao, V. J. *Thin Solid Films* **1985**, *127*, 85. (f) Cameron, D. C.; Irving, L. D.; Jones, G. R.; Woodward, J. *Thin Solid Films* **1982**, *91*, 339.

0897-4756/92/2804-0530$03.00/0

the development and practical application of new CVD source compounds for the deposition of aluminium and aluminum alloys is therefore an area of major concern.

Several organoaluminum precursors have been carefully investigated as CVD source materials. The most intensely studied are trimethylaluminum, $Al(CH_3)_3$ [TMA],[2,4] and triisobutylaluminum, $Al(i\text{-}C_4H_9)_3$ [TiBA].[5,6b] Most recently, the volatile donor–acceptor complexes of alane, $AlH_3\cdot(NR_3)_2$ (where R = CH_3 or CH_2CH_3, have been explored.[7,8] The alane adducts decompose through the initial dissociation of the Lewis base to generate alane, AlH_3, in situ.[8b] This decomposition pathway provides films with significantly lower carbon contamination although technological difficulties may still remain, including nucleation, alloying, and electronic property issues.[8a]

Besides binary and ternary aluminum-containing electronic structures, pure aluminum films are themselves of great interest for high density electronic media. One technological barrier to the utilization of aluminum thin films in this application arises from the electromigration of aluminum and the resulting formation of voids and hillocks in the films which leads to increased rates of device failure.[9] Aluminum alloy films which contain relatively small amounts of copper or silicon have been shown to exhibit significantly suppressed electromigration and spiking effects.[6] Recently, the incorporation of 0.002–0.8 wt % of boron in aluminum films was shown to completely stop aluminum electromigration and hillock formation.[10] These aluminum–boron alloys were shown capable of operating at high current densities (typically 10^6 A cm^{-2} at 175 °C) for prolonged periods without film degradation.[10a–f] The use of the boron-containing aluminum CVD source compounds presented in this paper allows the incorporation of boron directly into the deposited aluminum films, thus reducing electromigration effects and opening the pathway for the use of these source compounds in the formation of high current density devices.

The use of specifically designed boron cluster compounds which contain elements such as aluminum was expected to circumvent many of the problems encountered with the known source materials described above. In this paper we describe the first deposition chemistry and thin-film characterization of a variety of aluminum-containing polycrystalline thin films, including pure aluminum, alumina (Al_2O_3), and aluminum boride (AlB_n), from a new class of chemical vapor deposition source compounds, the aluminaboranes. These boron-based materials have the advantage of not containing any group IV elements strongly bonded to the metal, thus reducing the possibility of any group IV element incorporation into the deposited thin films. The boron-containing source materials described here are relatively thermally stable, volatile liquids that provide excellent precursor properties for CVD depositions. Finally, the deposition chemistry of this family of boron-containing precursor compounds may be extended to other main group depositions, such as gallium and indium. This is, in general, not possible for other classes of source compounds due to the difficulties encountered with the syntheses and instabilities of these compounds.[11]

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were recorded on a Cryomagnetics spectrometer operating at 80.26 MHz. Spectra were recorded in 5-mm tubes in both the ^1H coupled and decoupled modes and were externally referenced to BBr_3 at +40.0 ppm (positive chemical shifts indicate downfield resonances). Proton (^1H) NMR spectra were obtained on a General Electric QE-300 spectrometer operating at 300.15 MHz. Spectra were recorded on samples dissolved in $CDCl_3$ in 5-mm o.d. tubes with chemical shifts referenced to internal tetramethylsilane, with a positive shift indicating a resonance at a lower applied field than that of the standard. 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 either recorded in the gas phase or as Nujol mulls sandwiched between KBr plates. Scanning electron micrographs (SEM) were obtained on an ETEC autoscan instrument in the Center for Ultrastructure Studies of the S.U.N.Y. College of Environmental Science and Forestry (Syracuse, New York). Photographs were recorded on either Kodak Ektapan 4162 or Polaroid PN 55 film. X-ray emission spectra were obtained on a Kevex 7500 Microanalyst System. The X-ray diffraction spectra (XRD) were measured on a Phillips APD 3520 powder diffractometer equipped with a PW 1729 X-ray generator and a PW 1710 diffractometer control system. Cu Kα radiation and a graphite single-crystal monochromator were employed in the measurements reported here. The Auger electron spectra (AES) were measured on a Perkin-Elmer PHI 595 Scanning Auger Microprobe instrument in the Electronics Laboratory of General Electric Company, Syracuse, NY. 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/mm^2. The thicknesses of the films determined by AES depth profile measurements were performed by correlating experimental sputtering times to the sputtering times versus depth profiles for known thickness aluminum-con-

---

(4) (a) Motooka, T.; Fons, P.; Greene, J. E. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 345 and references therein. (b) Gow, T. R.; Lin, R.; Cadwell, L. A.; Lee, F.; Backman, A. L.; Masel, R. I. *Chem. Mater.* **1989**, *1*, 406. (c) Squire, D. W.; Dulcey, C. S.; Lin, M. *J. Vac. Sci. Technol., B* **1985**, *3*, 1513.

(5) (a) Bent, B. E.; DuBois, L. H.; Nuzzo, R. G. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 327. (b) Levy, R. A.; Green, M. L.; Gallagher, P. K. *J. Electrochem. Soc.* **1984**, *131*, 2175. (c) Green, M. L.; Levy, R. A.; Nuzzo, R. G.; Coleman, E. *Thin Solids Films* **1984**, *114*, 367. (d) Sekiguchi, A.; Kobayashi, T.; Hosokawa, N.; Asamak, T. *J. Vac. Sci. Technol. A* **1990**, *8*, 2976. (e) Bent, B. E.; Nuzzo, R. G.; DuBois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634. (f) Mantell, D. A. *J. Vac. Sci. Technol. A* **1989**, *7*, 630. (f) Dubois, L. H.; Zegarski, B. R.; Kao, C.-T.; Nuzzo *Surf. Sci.* **1990**, *236*, 77.

(6) (a) Vaidya, S.; Sinha, A. K. *Thin Solid Films* **1981**, *75*, 253. (b) Cooke, M. J.; Heinecke, R. A.; Stern, R. C.; Maes, J. W. C. *Solid State Technol.* **1982**, *25*, 62.

(7) Gladfelter, W. L.; Boyd, D. C.; Jensen, K. F. *Chem. Mater.* **1989**, *1*, 339.

(8) (a) Gross, M. E.; Cheung, K. P.; Fleming, C. G.; Kovalchick, J.; Heimbrook, L. A. *J. Vac. Sci. Tech. A* **1991**, *9*, 57. (b) Gross, M. E.; Fleming, C. G.; Cheung, K. P.; Heimbrook, L. A. *J. Appl. Phys.* **1991**, *69*, 2589. (c) Beach, D. B.; Blum, S. E.; LeGoues, F. K. *J. Vac. Sci. Technol., A* **1989**, *7*, 3117. (d) Hobson, W. S.; Harris, T. D.; Abernathy, C. R.; Pearton, S. J. *J. Appl. Phys. Lett.* **1991**, *58*, 77. (e) Dubois, L. H.; Zegarski, B. R.; Gross, M. E.; Nuzzo, R. G. *Surf. Sci.* **1991**, *244*, 89. (f) Roberts, J. S.; Button, C. C.; David, J. P. R.; Jones, A. C.; Rushworth, S. A. *J. Cryst. Growth* **1990**, *104*, 857. (g) Jones, A. C.; Rushworth, S. A. *J. Cryst. Growth* **1991**, *107*, 350. (h) Jones, A. C.; Rushworth, S. A. *J. Cryst. Growth* **1990**, *106*, 253. (i) Jones, A. C.; Rushworth, S. A.; Bohling, D. A.; Muhr, G. T. *J. Cryst. Growth* **1990**, *106*, 246. (j) Wee, A. T. S.; Murrell, A. J.; Singh, N. K.; O'Hare, D.; Foord, J. S. *J. Chem. Soc., Chem. Commun.* **1990**, 11.

(9) (a) Maissel, L. I.; Glang, R. *Handbook of Thin Film Technology*, McGraw-Hill: New York, 1970; pp 23–16. (b) Weast, R. C. *CRC Handbook of Chemistry and Physics*, CRC Press: Boca Raton, FL, 1979; p F-171.

(10) (a) Madokoro, S.; Tetsuda, H.; Umemura, E.; Sawada, S. Jpn. Patent 02297936, 1990; *Chem. Abstr.* **1991**, *114*, 219574w. (b) Sawada, S.; Kanano, O. Jpn. Patent 62240739, 1987; *Chem. Abstr.* **1988**, *109*, 15724g. (c) Sawada, S.; Kanano, O. Jpn. Patent 62235451, 1987; *Chem. Abstr.* **1988**, *108*, 178445k. (d) Sawada, S.; Kanano, O. Jpn. Patent 62235452, 1987; *Chem. Abstr.* **1988**, *108*, 178443h. (e) Sawada, S.; Kanano, O. Jpn. Patent 62240737, 1987; *Chem. Abstr.* **1988**, *108*, 117221n. (f) Sawada, S.; Kanano, O. Jpn. Patent 62240736, 1987; *Chem. Abstr.* **1988**, *108*, 117220m. (g) Dhaka, V. A.; Wajda, E. S. U.S. Patent 3355334, 1967; *Chem. Abstr.* **1968**, *68*, 82384u.

(11) (a) Wiberg, E.; Amberger, E. *Hydrides of the Elements of Main Groups I–IV*, Elsevier: New York, 1971 and references therein. (b) Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 1036. (c) Shriver, D. F.; Nordman, C. E. *Inorg. Chem.* **1963**, *2*, 1298.

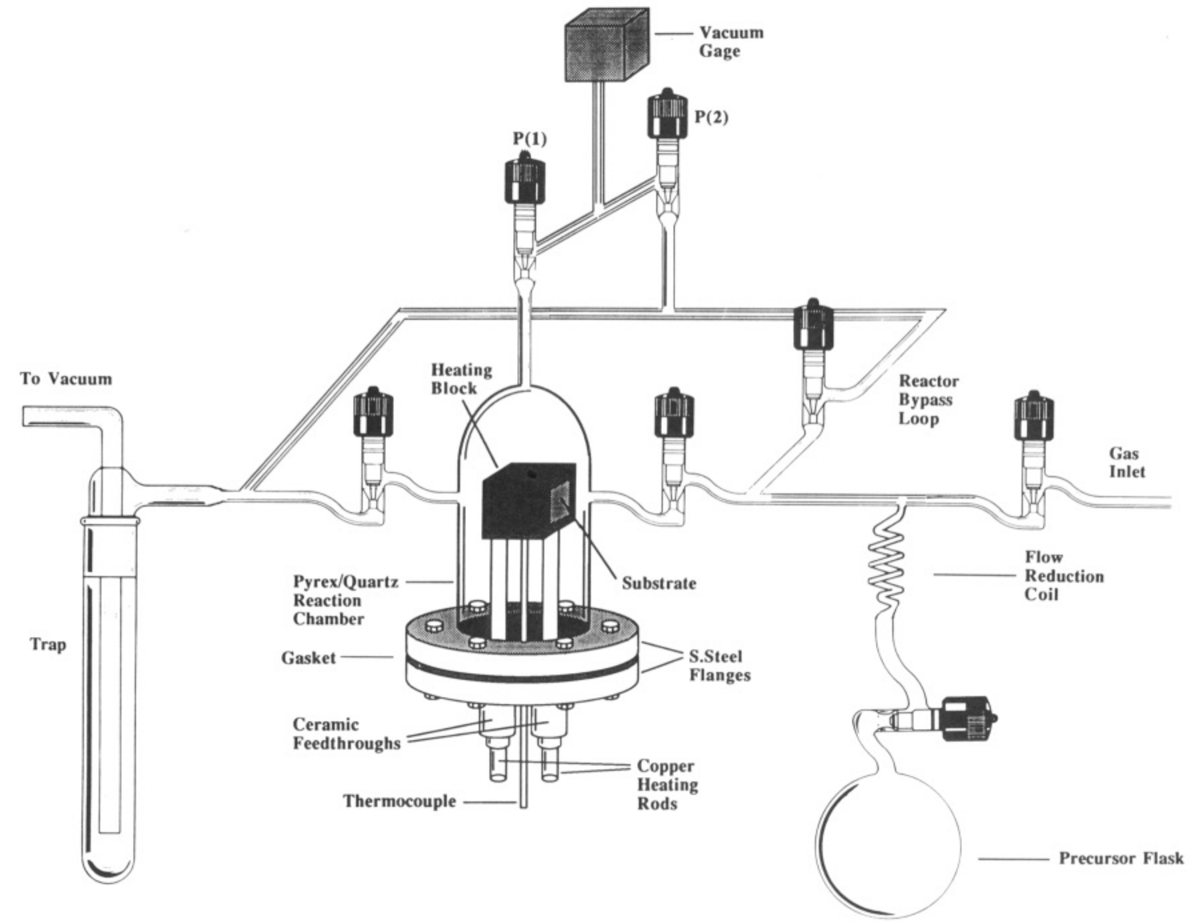

Figure 1. Experimental setup for the formation of aluminum thin film materials from boron-containing source compounds.

taining reference films. The concentrations of all elements except hydrogen and helium were measured in the spectra.

Materials. All solvents used were reagent grade or better. Diethyl ether was distilled from sodium metal prior to use. $CDCl_3$ was degassed by repeated freeze–thaw cycles and finally stored in vacuo prior to use. The aluminum borohydride, $Al(BH_4)_3$, **1**, (vapor pressure of 119.5 Torr at 0 °C, mp = −64.5 °C), was synthesized from the reaction of aluminum chloride and lithium borohydride using a modification of Schlesinger's method.[12] The $AlH_2(BH_4)\cdot N(CH_3)_3$, **2**, was prepared from the reaction of $AlH_2Cl\cdot N(CH_3)_3$ with $LiBH_4$.[13] Both compounds were characterized by multinuclear high-resolution NMR, mass and FT-IR spectroscopy and the results were compared to literature values, when available, to confirm the authenticity of the samples. The following commercially available (Aldrich) anhydrous chemicals were either used as received or purified by the method indicated and, where possible, were stored over 4-Å molecular sieves prior to use: aluminum chloride (triply sublimed from a mixture of $AlCl_3$ and dry NaCl), lithium borohydride, and trimethylamine hydrochloride.

Depositions. The depositions were performed in a medium-high vacuum apparatus (1×10^{-6} Torr ultimate vacuum) equipped with a standard pressure-sensing probe and a chromel-alumel thermocouple referenced to 0 °C. A schematic diagram for the experimental setup is shown in Figure 1. The substrates (1 cm × 2 cm) were mounted on a Mycor block and heated resistively via a tantalum wire embedded within the block. The entire heating-block assembly was mounted on a standard 2.75-in. stainless steel flange with ceramic feedthroughs. The flow of the source compound through the deposition cell and bypass loop was monitored throughout the reaction by pressure measurements at P(1) and P(2) (Figure 1). Control of the source flow in the system was achieved through the use of a flow reduction coil near the source reservoir, narrow-bore Teflon vacuum stopcocks (0–4 mm) and by cooling the precursor flask using an external slush bath to lower its vapor pressure.[14,15] In experiments in which a hydrogen carrier gas was used, the gas was first purified using standard O_2 and H_2O scrubbers, respectively, and the flow regulated by a single needle valve in the vacuum manifold. In a typical experiment, the precursor flask was charged with the source compound under inert conditions. The flask was attached to the vacuum manifold of the deposition system and cooled in an ethanol/dry ice slush bath (−78 °C) with the stopcock to the main manifold closed. The main vacuum system trap, located after the deposition chamber, was charged with dry, degassed acetone and cooled to −196 °C (to destroy any unreacted aluminum or boron-containing compounds which might pass through the system upon warming the trap to room temperature after completion of the deposition experiment). The entire reaction system was evacuated to 10^{-5} Torr. The substrate was heated to the desired temperature and allowed to reach thermal equilibrium. For experiments in which the substrate was pretreated with $TiCl_4$, the heated substrate was briefly exposed (1 min) to a vapor pressure of $TiCl_4$ from a cooled reservoir (10 °C) while pumping was maintained. Once the substrate reached equilibrium, the deposition chamber was closed off and the reactor bypass loop was opened. The flow of the source compound and carrier gas, if any, was then regulated to achieve a uniform flow through the bypass loop. Once the desired flow was established, the bypass loop was closed and the stopcocks to the deposition chamber were opened. The deposition was allowed to proceed until a silvery film was observed on the substrate. The stopcocks to the deposition chamber and precursor flask were then closed and the

---

[12] (a) Schlesinger, H. I.; Sanderson, R. T.; Burg, A. B. *J. Am. Chem. Soc.* **1940**, *62*, 3421. (b) Schlesinger, H. I.; Brown, H. C.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 209. (c) Brokaw, R. S.; Pease, R. N. *J. Am. Chem. Soc.* **1952**, *74*, 1590. (d) Badin, E. J.; Hunter, P. C.; Pease, R. N. *J. Am. Chem. Soc.* **1949**, *71*, 2950.

[13] Ruff, J. K. *Inorg. Chem.* **1963**, *2*, 515.

[14] Angelici, R. J. *Synthesis and Techniques in Inorganic Chemistry*; Saunders: Philadelphia, 1977; p 221.

[15] Gordon, A. J.; Ford, R. A. *The Chemists Companion: A Handbook of Practical Data, Techniques and References*; Wiley-Interscience: New York, 1972; p 451.

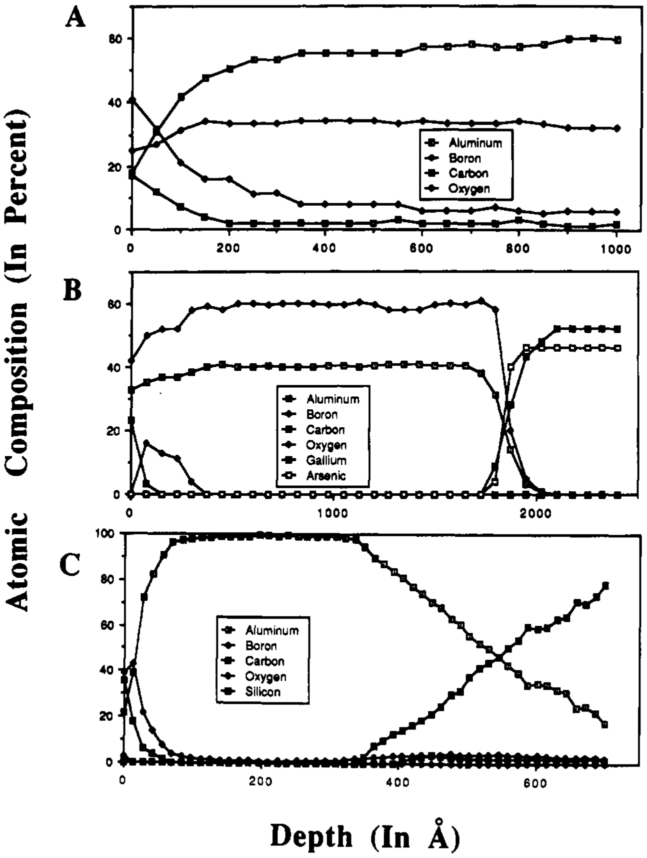

Figure 2. Representative Auger electron spectra (AES) for thin films deposited from boron-containing CVD precursors. The depth profiles were constructed from Auger electron spectra as the film was sputtered using Ar^+ ion milling. (A) Aluminum boride film deposited from $Al(BH_4)_3$, **1**, on copper. The substrate temperature during the deposition was 307 °C and the precursor reservoir was maintained at −78 °C throughout the deposition. (B) Aluminum oxide (Al_2O_3) film deposited from $Al(BH_4)_3$, **1**, on GaAs (100). The substrate temperature during the deposition was 332 °C and the precursor reservoir was maintained at −78 °C throughout the deposition. (C) Pure aluminum thin film deposited from $AlH_2(BH_4)\cdot N(CH_3)_3$, **2**, on Si (100) at room temperature. The substrate was pretreated with a brief exposure to $TiCl_4$ prior to the deposition.

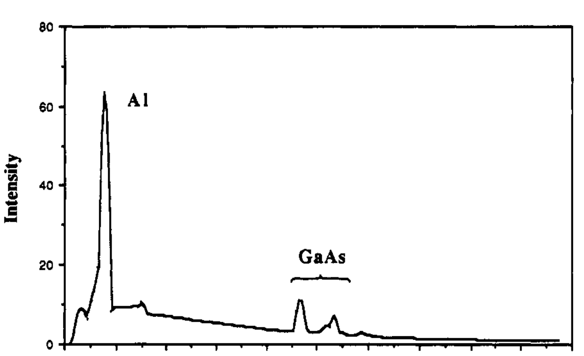

Figure 3. X-ray emission spectrum (XES) of the film deposited at 367 °C on GaAs (100) by the pyrolysis of aluminum borohydride, $Al(BH_4)_3$, **1**.

bypass opened. The substrate was allowed to cool slowly under vacuum to room temperature and the system was then evacuated. Once at room temperature, the chamber was opened directly to the air for removal of the samples.

Analysis. The films were analyzed by scanning electron microscopy (SEM), X-ray emission spectroscopy (XES), Auger electron spectroscopy (AES), and X-ray diffraction (XRD). The data for representative films are shown in Figures 2–5, respectively.

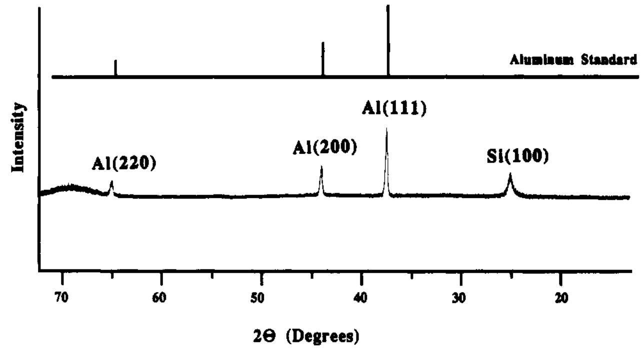

Figure 4. X-ray thin-film diffraction spectrum (XRD) for a pure aluminum film deposited from $AlH_2(BH_4)\cdot N(CH_3)_3$, **2**, on Si (100) at 132 °C without a $TiCl_4$ substrate pretreatment. The literature data for a polycrystalline aluminum standard are plotted above the XRD spectrum for the film from **2**.[16] The peak at 26.38° is due to the Si (100) reflection of the substrate.

For the SEM and XES studies of a film, the substrate containing the deposited film was mounted on an aluminum stub with double-sided tape, and the edges were coated using carbon paint to provide a conductive contact between the sample and the aluminum stub. Rough aluminum compositions were determined by measuring the intensity of the aluminum signal of the sample in the XES and interpolating this value to an aluminum composition using a standard XES calibration curve.[16a] The standards were first analyzed by Auger electron spectroscopy (AES) and the intensity of the aluminum peak measured in the XES. A plot of XES aluminum signal intensity versus percent aluminum (by AES) gave a 98.5% (*R*) correlation calibration curve.[16a] The intensities of the aluminum peak in the XES for samples of unknown composition were then measured and percentages determined using the calibration plot. The thickness measurements from the XES data were determined by varying the beam energy in the SEM and observing the XES for the detection of peaks due to the substrate. The energy at which the substrate signal was found to disappear was then used in the Kanaya–Okayama formula range to determine the film thicknesses.[17] The thicknesses of the films were also determined by AES depth profile measurements as described above.

Results and Discussion

The search for a greater understanding of the deposition chemistry of CVD precursor compounds and the identification of potential new families of organometallic and main-group precursors for application to MOCVD or MOMBE technology is critical to the continued development of new thin-film materials. The use in CVD of designed molecular precursors which allows unique control of film composition in the CVD formation has recently been demonstrated.[16,18] Among the newest family of

---

(16) (a) Glass, J. A., Jr.; Kher, S.; Hersee, S. D.; Ramseyer, G. O.; Spencer, J. T. *Mater. Res. Soc. Symp. Proc.* **1991**, *204*, 397. (b) Amini, M. M.; Fehlner, T. P.; Long, G. J.; Politowski, M. *Chem. Mater.* **1990**, *2*, 432. (c) Kim, Y.-G.; Dowben, P. A.; Spencer, J. T.; Ramseyer, G. O. *J. Vac. Sci. Technol. A* **1989**, *7*, 2796. (d) Mazurowski, J.; Baral-Tosh, S.; Ramseyer, G.; Spencer, J. T.; Kim, Y.-G.; Dowben, P. A. *Mater. Res. Soc. Symp. Proc.* **1991**, *190*, 101. (e) Dowben, P. A.; Spencer, J. T.; Stauf, G. T. *Mater. Sci. Eng. B* **1989**, *B2*, 297. (f) Glass, J. A., Jr.; Kher, S.; Kim, Y.-G.; Dowben, P. A.; Spencer, J. T. *Mater. Res. Soc. Symp. Proc.* **1991**, *204*, 439. (g) Zhang, Z.; Kim, Y. G.; Dowben, P. A.; Spencer, J. T. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 407.

(17) Goldstein, J. I.; Newbery, D. E.; Echlin, P.; Joy, D. C.; Fiori, C.; Lifshin, E. *Scanning Electron Microscopy X-Ray Microanalysis*; Plenum Press: New York, 1981; p 72.

(18) (a) Gross, M. E., Jasinski, J. M., Yates, J. T., Jr., Eds. *Chemical Perspectives of Microelectronic Materials*; Materials Research Society: Pittsburgh, PA, 1989. (b) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248. (c) Jeffries, P. M.; Girolami, G. S. *Chem. Mater.* **1989**, *1*, 8. (d) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 1643. (e) Gozum, J. E.; Girolami, G. S. *J. Am. Chem. Soc.* **1991**, *113*, 3829.

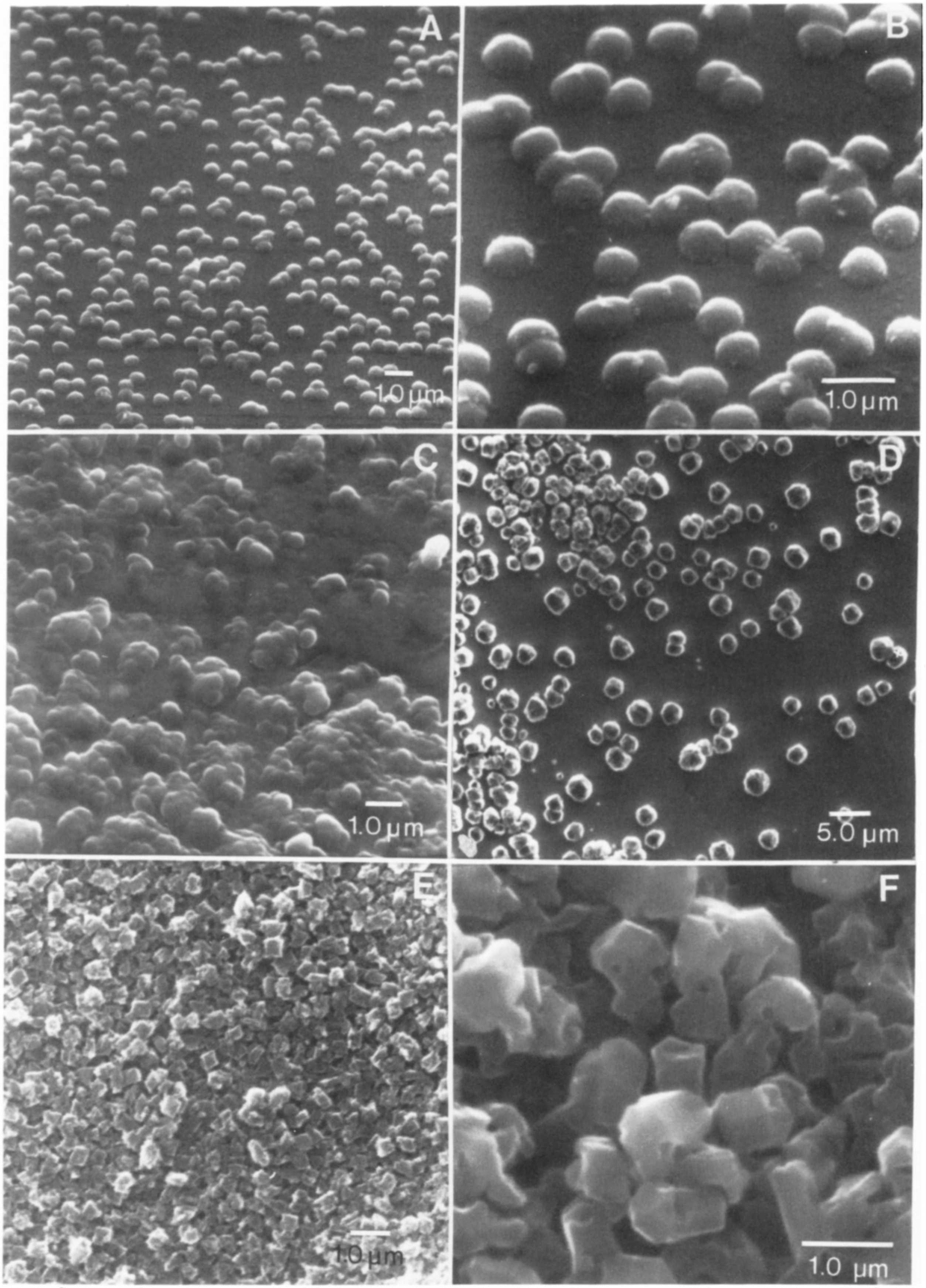

Figure 5. Scanning electron micrographs (SEM) of thin films deposited from boron-containing CVD precursors. The bars in the lower right corners of each photograph indicate scale. (A) A very thin aluminum boride film deposited from $Al(BH_4)_3$, **1**, at 332 °C on GaAs (100) [magnification 3000×], (B) magnification of a very thin aluminum boride film deposited from $Al(BH_4)_3$, **1**, at 367 °C on GaAs (100) [magnification 10 000×], (C) aluminum boride film deposited from $Al(BH_4)_3$, **1**, at 332 °C on GaAs (100) [magnification 5000×], (D) a very thin pure aluminum film deposited from $AlH_2(BH_4)\cdot N(CH_3)_3$, **2**, at 121 °C on Si (100) following a $TiCl_4$ substrate pretreatment [magnification 500×], (E) pure aluminum thin film deposited from $AlH_2(BH_4)\cdot N(CH_3)_3$, **2**, at 127 °C on GaAs (100) following a $TiCl_4$ substrate pretreatment [magnification 1000×], and (F) pure aluminum thin film deposited from $AlH_2(BH)_4\cdot N(CH_3)_3$, **2**, at 99 °C on Si (100) following a $TiCl_4$ substrate pretreatment [magnification 15 000×].

Table I. Selected Deposition Data for Typical Aluminum Containing Thin Films Derived from Boron-Containing Precursor Compounds

film no.	source	substrate	substrate temp[a]	source temp[a]	amt, %				carrier	pretreatment	analysis[b]	grain size[f]	depn rate[g]
					Al	B	O	C					
					Aluminum Boride								
1	$Al(BH_4)_3$	Cu	428	−78	49.1	33.6	12.1	5.2	none	H_2/N_2	AES	0.5	10.2 (>29.5)
2	$Al(BH_4)_3$	Cu	307	−78	55.5	34.1	5.4	5.0	none	H_2/N_2	AES	0.4	1.7 (>8.3)
3[e]	$Al(BH_4)_3$	Cu	367	−63.5	19.0	72.0	9.0	0.0	none	H_2/N_2	AES	0.5	21.6 (49.8)
4	$Al(BH_4)_3$	GaAs[d]	367	−78	54.5				none	none	XES	0.4	
5	$Al(BH_4)_3$	SiO_2	317	−72	76.9				none	none	XES		3.7
6	$Al(BH_4)_3$	GaAs[d]	332	−78	24.8				none	H_2/N_2	XES	0.6	5.1
					Aluminum Oxide								
7	$Al(BH_4)_3$	GaAs[d]	332	−78	40.0	0.0	60.0	0.0	none	none	AES		12.3 (43.0)
					Pure Aluminum								
8	$AlH_2(BH_4){\cdot}L$[c]	Si(100)	25	25	99.4	0.0	0.0	0.0	none	$TiCl_4$	AES		(2.0)
9	$AlH_2(BH_4){\cdot}L$[c]	Teflon	25	25	99.4	0.0	0.0	0.0	none	$TiCl_4$	AES		
10	$AlH_2(BH_4){\cdot}L$[c]	Mycor	116	25	97.4				none	none	XES	3.0	
11	$AlH_2(BH_4){\cdot}L$[c]	GaAs[d]	127	25	95.0				none	$TiCl_4$	XES	0.3	7.9
12	$AlH_2(BH_4){\cdot}L$[c]	SiO_2	99	25	99.3				none	$TiCl_4$	XES	0.3	338.6

[a] In °C. [b] AES = Auger electron spectroscopy; XES = X-ray emission spectroscopy. [c] L = $N(CH_3)_3$. [d] GaAs (100). [e] Annealed film at 617 °C for 1.5 h followed by 672 °C for 0.5 h. [f] Grain size in μm, as determined from SEM. [g] The deposition rate is given in Å min^{-1} using film thicknesses estimates from XES measurements and assuming the experimental film density was equal to that of pure aluminum. The values in parentheses are deposition rates determined from AES measurements.

precursor compounds to be investigated for CVD applications for the formation of a wide variety of thin films are the boron-containing compounds.[16,18d] In this paper we report the results of our investigations into the formation of thin films of pure aluminum, aluminum boride and alumina from the aluminaborane compounds, $Al(BH_4)_3$, **1**, and $AlH_2(BH_4){\cdot}N(CH_3)_3$, **2**. Selected deposition data and experimental parameters for the formation of typical aluminum-containing thin films from these boron-containing precursor compounds are given in Table I. Representative AES, XES, XRD, and SEM spectra for these films are shown in Figures 2–5, respectively.

For each of the new source compounds investigated in this paper, thin films were readily prepared by using the low-pressure chemical vapor deposition (LPCVD) reactor system shown in Figure 1. In each case, film thicknesses and deposition rates were controlled by the modulation of several readily regulated deposition parameters including precursor flow rate into the cell, substrate temperature, precursor exposure times to the substrate, and the nature of substrate pretreatment. In general, film thicknesses ranged from 500 to 20 000 Å, depending on the deposition parameters employed. Flow and deposition rates were kept rather small (Table I) for the work reported here in order to achieve greater control in the small reactor system employed. Polycrystalline films were readily formed at relatively low temperatures, even at room temperature with the use of compound **2** and a $TiCl_4$ pretreated substrate, thus allowing the formation of thin films from these new precursors on thermally sensitive substrates such as plastics. The direct pyrolysis of the source compound on the substrate was observed in each instance by noting the decrease in the thickness of the film as the distance from the precursor orifice to the substrate increased.[16b] The boron-containing precursors **1** and **2** are very volatile, colorless air-sensitive liquids which can be readily prepared in high purity. Compound **2** is stable indefinitely at room temperature and is nonpyrophoric. To demonstrate the deposition chemistry of these new source compounds in providing clean thin-film materials, polycrystalline films of pure aluminum, aluminum boride, and aluminum oxide were prepared and characterized. The thin-film formation and characterization for each of these aluminum-based materials is presented below separately.

Pure Aluminum Thin Films. Pure aluminum thin films were grown from $AlH_2(BH_4){\cdot}N(CH_3)_3$, **2**, on a variety of substrates including Si(100), GaAs(100), SiO_2(100), Teflon, and Mycor. In the deposition of the films, effective control over the delivery of the source compound to the substrate was maintained through the use of a glass capillary flow reduction coil, Figure 1. Typical deposition data for the aluminum films prepared from **2** are given in Table I. The deposition of aluminum films from trialkylaluminum and alane trimethylamine sources employing a brief substrate pretreatment with $TiCl_4$ has been reported. In these depositions, the film morphologies have been significantly improved, presumably by modifying the initial nucleation characteristics of the film on the substrate.[4,7,8] In our experiments using compound **2** without a $TiCl_4$ substrate pretreatment, thin-film formation was not observed until a minimum substrate temperature of approximately 100 °C was achieved. Pretreatment of the substrate with a very short exposure of $TiCl_4$ (<1 min), however, resulted in the rapid formation of pure polycrystalline aluminum films on plastic and other temperature-sensitive substrates at room temperature. Thus, the onset temperature of film growth can be effectively controlled by the manner in which the substrate is prepared prior to deposition. The films, both with and without the $TiCl_4$ pretreatment, were very uniform in appearance, very highly specular and indefinitely air stable. The low resistivity values measured for these films were similar to those reported for pure aluminum films prepared from evaporation techniques (Al film resistivity; measured = $(2.0 \pm 1) \times 10^{-6}\ \Omega$ cm, literature = $2.6 \times 10^{-6}\ \Omega$ cm).[7,9b] The measured resistivities for the CVD films from **2** and the standard films were within experimental error of each other, given the uncertainty in the film thickness measurements (as determined from AES depth profile data).

X-ray emission spectroscopic (XES) data were measured for the aluminum films prepared from **2** without $TiCl_4$ substrate pretreatment. The spectra showed clearly only the intense signals from aluminum at 1.487 keV ($K\alpha_1$) and those signals which arise from the substrate. Since the film compositions for boron and the other lighter elements were not obtainable directly from the XES spectra, the Auger electron spectra (AES) were measured to determine the complete film composition as a function of film depth. The results of the Auger electron depth profile of a typical film grown on a Si (100) substrate are shown in Figure 2C. The surface layer was found to be contaminated with oxygen and carbon from atmospheric exposure prior to the spectral measurements but dropped to within the AES detection limits very rapidly. No signals for chlorine or titanium were observed in the AES for samples in which the substrate had been pretreated with a $TiCl_4$ exposure. This is consistent with the results obtained by Gladfelter[7] and Cooke,[6] who report that less than a monolayer of $TiCl_4$ adsorbs to the substrate during the pre-treatment step. No boron was detected in the sample (apart from a 3% surface contamination which dropped to the detection limit of AES within 20 Å of the surface). The aluminum composition for the bulk sample approached 100%. The film also appeared to be very uniform in composition as a function of depth.

X-ray diffraction data (XRD) for the aluminum films clearly show the formation of polycrystalline aluminum materials. The XRD spectrum for a typical film grown on a Si (100) substrate without a $TiCl_4$ pretreatment is shown in Figure 4. The XRD spectrum showed only the expected peaks and intensities for a polycrystalline aluminum film relative to the standard (with no other peaks observed other than those from the substrate).[19a] The observed 2θ angles (in degrees), relative peak intensities and peak assignments for polycrystalline aluminum thin films in the CVD samples relative to the standard literature values were (using Cu Kα radiation) 38.00° ($2\theta_{\text{lit.}}$ = 38.56°, Al(111), I = 100, I_{strd} = 100), 44.55° ($2\theta_{\text{lit.}}$ = 44.86°, Al(200), I = 47, I_{strd} = 47), and 64.95° ($2\theta_{\text{lit.}}$ = 65.13°, Al(220), I = 23, I_{strd} = 22). Similar data were obtained from the CVD aluminum films on other substrates (Table I).

The microstructure of the pure aluminum films was investigated by using scanning electron microscopy (SEM). Shown in Figure 5D–F are typical SEM photomicrographs for films grown at several temperatures on Si (100) and GaAs (100) substrates following a $TiCl_4$ pretreatment. Shown in Figure 5D is a very thin film in which the substrate was only very briefly exposed to the compound 2. Apparently, the initially small crystallites of aluminum form the nucleation sites for the formation of the thicker films shown in Figure 5E. The grain sizes in these films were uniform with an average size of 0.28 μm. This value compares well with the average crystallite size of 0.15 μm for the CVD aluminum films previously reported by Gladfelter.[7] The polycrystalline nature of these mirrorlike films is evident from Figure 5E. Aluminum films deposited on substrates without a $TiCl_4$ pretreatment showed grain sizes significantly larger than those grown on pretreated substrates with an average grain size of 3 μm. It appears that for the pretreated surfaces the rate of nucleation is greater than the rate of crystal growth. For films grown without a surface pretreatment, the rate of crystal growth is larger than the nucleation rate. Similar trends have been reported previously.[7]

Aluminum Boride Thin Films. The synthesis of the first member of the aluminaborane family, aluminum borohydride, $Al(BH_4)_3$, 1, was initially reported over 50 years ago by Schlesinger.[12] The use of this compound for the CVD deposition of aluminum-containing thin films was presented in a preliminary report.[16a] Compound 1, first prepared from the reaction of trimethylaluminum and diborane(6),[12a] is readily synthesized in essentially quantitative yields as a very pure material from the reaction of aluminum trichloride with alkali-metal borohydrides in a solid-state reaction at 100 °C.[12b] The compound, which is rather stable under vacuum[12b,c] and can be readily purified by vacuum trap-to-trap distillation,[20] reacts violently with moist air.[12d] The compound may be stabilized, however, by adsorption on lithium bromide.[21] Free 1 may be regenerated by heating the mixture under vacuum.[21]

Uniform thin films of aluminum boride were readily prepared from the CVD deposition of 1 at temperatures above 300 °C on a variety of substrates. In the formation of the aluminum boride films, control over the flow of the source compound to the deposition chamber was maintained through the use of a source reservoir cooling bath (external) and a glass capillary flow reduction coil. Significantly faster deposition rates were, however, readily achieved by using either a higher temperature bath or by simply shortening or eliminating the flow reduction coil. Typical data for these films are given in Table I. The films were typically grayish in color and adhered very well to the substrates (tape test).

The elemental compositions of films grown from 1 were characterized by XES and AES techniques. The results of the XES and Auger electron depth profile of a typical film grown on a copper substrate are shown in Figures 3 and 2a, respectively. The XES showed only peaks corresponding to the aluminum Kα_1 emission and peaks from the GaAs substrate, similar to that observed for the pure aluminum films deposited from 2. The AES spectrum, however, showed the presence of approximately 34% boron in the films as a metal boride. The films were very uniform in composition throughout the bulk of the sample. The surface layer was contaminated with oxygen and carbon from the post-deposition atmospheric exposure of the film and this contamination dropped very rapidly to rather low values. Film compositions ranging from approximately 24% to 71% aluminum were readily obtained by varying the deposition conditions, Table I.

SEM photomicrographs of several aluminum boride films are shown in Figure 5A–C. Parts A and B show very thin aluminum boride films prepared from the decomposition of 1 on monolithic GaAs(100). During the deposition, the substrate was heated to 332 °C and a small source flow was maintained during the deposition by cooling the source reservoir to −78 °C to produce a very thin material. The small "droplets" are the aluminum boride material deposited on the substrate. When the vapor-phase concentration of the aluminum borohydride is significantly increased and thicker films are prepared, continuous conformal films are obtained (Figure 5C). It appears that the initial spheres of the epitaxial growth coalesce into the uniform thin film observed. The thicker films still retain a resemblance to the semispherical droplets observed in the thinner films. Film thicknesses ranging between 100 Å and 2 μm were easily prepared by modifying the precursor flow rate and the deposition time. The films appeared to be noncrystalline from XRD experiments.

The binary phase diagram for the aluminum–boron system indicates that films deposited below approximately 659 °C should consist of a mixture of pure aluminum and the AlB_2 phase.[19b,c] Calculations indicate that for the films deposited from compound 1, the composition typically obtained was 90.0% AlB_2 and 10.0% pure aluminum. Previous work[19b,c] has shown that the pure aluminum liberated during the deposition has a strong tendency to

---

(19) (a) Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, Card No. 4-0787. (b) Sirtl, E.; Woerner, L. M. *J. Cryst. Growth* **1972**, *16*, 215. (c) Serebryanskii, V. T.; Epel'baum, V. A ; Zhdanov, G. S. *Dokl. Akad. Nauk SSR* **1961**, *141*, 884.

(20) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, Wiley-Interscience: New York, 1986; pp 190–200.

(21) Wiberg, E.; Neumeier, U. Ger. Patent 1080527, 1960.

form small droplets. This droplet formation is consistent with the SEM observations of the relatively thin films deposited.

Aluminum Oxide (Alumina, Al_2O_3) Thin Films. The deposition of alumina (Al_2O_3) thin films was achieved by admitting a small partial (10^{-3} Torr) pressure of oxygen into the deposition chamber during the deposition with compound 1. The films thus obtained appeared matte white due to a relatively rough surface morphology, as observed in the SEM. The films were again found to adhere very well to the substrate surface.

The AES depth profile for a typical alumina film is shown in Figure 2B. The profile shows the uniform composition of the film corresponding to the Al_2O_3 stoichiometry. The surface has a small amount of carbon contamination which decreased very rapidly to the detection threshold. The surface of the film also shows some boron contamination, presumably due to residual $Al(BH_4)_3$ in the deposition chamber after the completion of the deposition; the boron content also decreased very rapidly in the bulk sample.

X-ray diffraction data (XRD) for the alumina films show the formation of polycrystalline materials. The XRD spectrum showed the expected peaks and intensities for polycrystalline alumina relative to the standard.[22] The observed 2θ angles (in degrees), relative peak intensities, and peak assignments for polycrystalline alumina thin films in the CVD samples relative to the standard literature values (using Cu Kα radiation) were 31.81° ($2\theta_{\text{lit.}}$ = 31.45°, Al_2O_3(122, 215)), and 66.35° ($2\theta_{\text{lit.}}$ = 67.19°, Al_2O_3(004)).

The microstructure of the alumina films showed a surface structure very similar to that observed for the aluminum boride films. Initial "droplet" nucleation sites in the very thin films were found to grow into conformal materials in the thicker films.

Conclusions

The absence of boron contamination in the films formed from complex 2 suggests that one possible mode for its decomposition is the initial formation of $BH_3{\cdot}N(CH_3)_3$ followed by the loss of H_2 and the formation of metallic aluminum, shown in eqs 1–4. This proposed mechanism

$$AlH_2(BH_4){\cdot}NMe_3(g) \rightarrow AlH_3(g) + BH_3{\cdot}NMe_3(g) \quad (1)$$

$$AlH_3(g) + 2Al(s) \rightarrow 3AlH(s) \quad (2)$$

$$AlH_2(BH_4){\cdot}NMe_3(g) \rightarrow AlH + BH_3{\cdot}NMe_3(g) + H_2 \quad (3)$$

$$3AlH(s) \rightarrow {}^3/_2H_2 + 3Al(s) \quad (4)$$

of aluminum deposition on aluminum surfaces is supported by the experimental observation of the formation of $BH_3{\cdot}N(CH_3)_3$ from the thermal decomposition of 2.[13] The facile elimination of $BH_3{\cdot}N(CH_3)_3$ from 2 would also be anticipated based upon the known structure of 1 in which the two Al–H–B bridges of each $AlBH_4$ unit are asymmetric; with one bridging hydrogen atom closer to the aluminum center and one closer to the boron atom.[23] Whether alane or AlH are formed as intermediates in the first step (eqs 1 and 3, respectively) is, at this point, unclear. It does appear, however, that the presence of at least one hydrogen atom on the aluminum center is critical for the clean elimination of $BH_3{\cdot}N(CH_3)_3$ and the deposition of aluminum since for all the depositions from compound 1 (in the absence of oxygen), aluminum boride rather than pure aluminum films were formed. The deposition mechanism for compound 2 appears to be superior to the β-hydride elimination process thought to be important for the trialkylaluminum sources in providing pure thin films.[24] This is presumably due to the fact that the "active" intermediate from 2 contains no organic groups. The mechanism reported for the deposition of aluminum from the alane trimethylamine adduct, $AlH_3{\cdot}(NMe_3)_2$, suggests that the initial steps involve the dissociation of the two trimethylamino groups from the alane.[5f,7] Previous studies have indicated that the dissociation of trimethylamine ligands from $AlH_3{\cdot}(NMe_3)_2$ precedes hydrogen loss.[25] After the gas-phase ligand dissociation steps, the alane is proposed to adsorb onto the aluminum surface to produce AlH(s) species. The final step is the loss of hydrogen from the AlH surface. Hydrogen desorption studies from aluminum surfaces have shown that H_2 desorbs around 60 °C.[5a,26] Thin-film formation was not observed, however, from $AlH_3{\cdot}(NMe_3)_2$ until 100 °C and no film formation was observed at room temperature.[7] It was therefore impossible to decide unambiguously between the initial ligand dissociation step or the final hydrogen desorption step as to which was the rate-limiting process. In the depositions from compound 2, pure aluminum thin films were readily prepared at room temperature. Thus for depositions from compound 2, it appears that the desorption of hydrogen from the aluminum surface may not be the rate-limiting step for deposition but rather that the $BH_3{\cdot}N(CH_3)_3$ dissociation process is the slow step. Kinetic studies to further elucidate the mechanism of aluminum deposition from these boron-containing source compounds and the critical role $TiCl_4$ plays in the process are planned.

The very high-volatility, variable-temperature deposition threshold (25 °C with $TiCl_4$ and 100 °C without $TiCl_4$) and high chemical stability of 2 suggests that it should be an excellent MOCVD and MOMBE precursor for pure aluminum films, circumventing many of the problems seen in other aluminum sources. In fact, the new source compounds investigated here were typically so volatile that difficulties were initially experienced in keeping the flow rate of the source compound small enough to allow for reasonable control of the deposition parameters in the relatively small CVD system employed in this work. Thus, it was found necessary to control the flow of the source with a source reservoir cooling bath and a glass capillary flow reduction coil to keep the deposition rate to between 10 and 500 Å min^{-1}.

The formation of very high quality thin films from source compounds belonging to this family of boron-containing precursor compounds should be extendable to other main-group depositions, such as gallium and indium. This is, in general, not possible for other classes of sources due to the difficulties encountered with the syntheses and instabilities of the compounds.[11]

Our current and future work is directed toward investigations into the deposition mechanisms of new thin film materials using these and other members of the boron-containing class of CVD source compounds. In addition, we are exploring the application of these sources to the formation of materials such as $Al_xGa_{1-x}As$ and related systems. These studies are designed to provide further insights into the deposition chemistry of these source

---

[22] Fang, J. H.; Bloss, F. D. *X-ray Diffraction Tables*; S. Illinois Press: London, 1966.

[23] (a) Almenningen, A.; Gundersen, G.; Haaland, A. *Acta Chem. Scand.* **1968**, *22*, 328. (b) Bauer, S. H. *J. Am. Chem. Soc.* **1950**, *72*, 622.

[24] Zanella, P.; Rossetto, G.; Brianese, N.; Ossola, F.; Porchia, M.; Williams, J. O. *Chem. Mater.* **1991**, *3*, 225.

[25] Nechiporenko, G. N.; Petukhova, L. B.; Rozenberg, A. S. *Izv. Akad. Nauk SSR, Ser. Khim.* **1975**, 1697.

[26] Paul, J.; Hoffmann, F. M. *Surf. Sci.* **1988**, *194*, 419.

compounds and to elucidate the important factors for determining the suitability of a source compound for the formation of desirable thin film materials.

Acknowledgment. We thank Dr. Stephen D. Hersee and Mr. George O. Ramseyer for their technical assistance and valuable discussions during the course of this work. We thank the National Science Foundation (Grant No. MSS-89-09793), International Business Machines, the General Electric Co., and the Wright-Patterson Laboratory (Award No. F33615-90-C-5291) for support of this work.

Registry No. Al, 7429-90-5; AlBn, 37367-77-4; Al_2O_2, 1344-28-1; $Al(BH_4)_3$, 13771-22-7; $AlH_2(BH_4)\cdot N(CH_3)_3$, 92275-85-9.

Chemical Vapor Deposition Precursor Chemistry. 3. Formation and Characterization of Crystalline Nickel Boride Thin Films from the Cluster-Assisted Deposition of Polyhedral Borane Compounds[1]

Shreyas S. Kher and James T. Spencer*

Department of Chemistry and the Center for Molecular Electronics, Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100

Received July 22, 1991. Revised Manuscript Received February 10, 1992

The deposition of both metal-rich and boron-rich thin-film phases of nickel boride from boron-containing precursor compounds by a cluster deposition process is reported. The thin films were characterized by EDXA, AES, SEM, XRD, FT-IR, TEM, and electron diffraction experiments. The films were shown by AES to be compositionally uniform in the bulk sample. Film thicknesses up to 3 μm were readily prepared by controlling the flow rate of the borane into the cell, the substrate temperature, and the duration of the deposition. The stoichiometric composition of the films was controlled by regulating the deposition temperature, the borane flow rate into the reactor, and the base vacuum conditions during the film formation. A relationship was found to exist between the temperature during deposition and the film composition with a maximum nickel content reached at approximately 530 °C. The effect of annealing both the nickel-rich and the boron-rich films was studied by SEM, XRD, and electron diffraction experiments. SEM data for the annealed boron-rich films showed the formation of perfect hexagonal crystals in a channelled columnar matrix. Electron diffraction data showed that this crystalline phase is hexagonal Ni_7B_3 isolated in a Ni_3B matrix. The as-deposited nickel-rich films were found by XRD studies to be primarily pure nickel, containing relatively small amounts of the Ni_3B phase relative to the pure nickel phase. This has been attributed to the precipitation of boron-rich phases as very small crystallites at the grain boundaries of the pure nickel material. XRD spectra for the boron-rich films showed that the films consisted of Ni_3B with no pure nickel observed. Annealing of these films did not result in the formation of pure nickel phases in the XRD spectra.

Introduction

In recent years, the formation of transition metal boride thin films has received increasing research attention. Interest in the preparation,[2] theoretical modeling,[3] and solid-state characteristics[4] of these metal borides is primarily due to their unique physical properties among solid-state materials and to their wide structural diversity. Metal borides are typically extremely refractory materials, frequently with melting points far in excess of that found for the pure metal. In addition, they are exceptionally hard materials which are resistant to attack even in the most harsh chemical environments.[4] The transition metal borides are also known to be good electrical conductors, with resistivities occasionally lower than the corresponding pure metals (i.e., LaB_6), and some even become superconducting at low temperatuers. Thus, metal borides have found increased use not only in traditional applications such as hard coatings for cutting tools[5] but also in thermally and chemically taxed aerospace components,[6] high-energy optical systems,[7] thermionic emitters, and new magnetic materials.[8]

---

(1) Part 1: Glass, J. A., Jr.; Kher, S.; Spencer, J. T. *Thin Solid Films* **1992,** *207,* 15. Part 2: Glass, J. A., Jr.; Kher, S. S.; Spencer, J. T. *Chem. Mater.*, previous paper in this issue.

(2) (a) Thompson, R. *Prog. Boron Chem.* **1970,** *2,* 173. (b) Schwarzkopf, P.; Kieffer, R.; Leszynski, W.; Benesovsky, K. *Refractory Hard Metals, Borides, Carbides, Nitrides, and Silicides*; MacMillan: New York, 1953. (c) Aronsson, B.; Lundstrom, T.; Rundqvist, S. *Borides, Silicides and Phosphides*; Wiley: New York, 1965. (d) *Boron and Refractory Borides*; Matkovick, V. I., Ed.; Springer-Verlag: New York, 1977. (e) Samsonov, G. V.; Goryachev, Y. M.; Kovenskaya, B. A. *J. Less.-Common Met.* 1976, *47,* 147. (f) Lipscomb, W. N. *J. Less.-Common Met.* 1981, *82,* 1. (g) Etourneau, J.; Hagenmuller, P. *Philos. Mag.* **1985,** *52,* 589.

(3) (a) Minyaev, R. M.; Hoffmann, R. *Chem. Mater.* **1991,** *3,* 547. (b) Burdett, J, K.; Canadell, E. *Inorg. Chem.* **1988,** *27,* 4437. (c) Mohn, P.; Pettifor, D. G. *J. Phys. C: Solid State Phys.* **1988,** *21,* 2829. (d) Mohn, P. *J. Phys. C: Solid State Phys.* **1988,** *21,* 2841. (e) Burdett, J. K.; Canadell, E.; Miller, G. J. *J. Am. Chem. Soc.* **1986,** *108,* 6561. (f) Pettifor, D. G.; Podloucky, R. *J. Phys. C: Solid State Phys.* **1986,** *19,* 315. (g) Armstrong, D. R. *Theor. Chim. Acta* **1983,** *64,* 137. (h) Armstrong, D. R.; Perkins, P. G.; Centina, V. E. *Theor. Chim. Acta* **1983,** *64,* 41. (i) Ihara, H.; Hirabayashi, M.; Nakagawa, H. *Phys. Rev. B: Solid State Phys.* **1977,** *B16,* 726. (j) Perkins, P. G.; Sweeney, A. V. J. *J. Less.-Common Met.* **1976,** *47,* 165. (k) Liv, S. H.; Koop, L.; England, W. B.; Myron, H. W. *Phys. Rev. B: Solid State Phys.* **1975,** *B11,* 3463.

(4) Samsonov, G. V. *Handbook of High-Temperature Materials, No. 2 Properties Index*; Plenum Press: New York, 1964.

(5) (a) Mullendore, A. E.; Pope, L. W. *Thin Solid Films* **1987,** *153,* 267. (b) Skibo, M.; Greulich, F. A. *Thin Solid Films* **1984,** *113,* 225. (c) Campbell, A. N.; Mullendore, A. W.; Hills, C. R.; Vandersande, J. B. *J. Mater. Sci.* **1988,** *23,* 4049.

(6) (a) Patterson, R. J. U.S. Patent No. 3, 499,799, 1970. (b) Lewandowski, R. S. U.S. Patent No. 4,522,849, 1985. (c) Branovich, L. E.; Fitzpatrick, W. B. P.; Long, M. L.; Jr. U.S. Patent No. 3,692,566, 1972.

(7) Knittl, Z. *Optics of Thin Films*; Wiley and Sons: New York, 1976.

(8) (a) Bakonyi, I. *J. Magn. Magn. Mater.* **1988,** *73,* 171. (b) Mutlu, R. H.; Aydinuraz, A. *J. Magn. Magn. Mater.* **1987,** *68,* 328. (c) Lundquist, N.; Myers, H. P.; Westin, R. *Philos. Mag.* **1962,** *7,* 1187. (d) Kaul, S. N.; Rosenberg, M. *Phys. Rev.* **1982,** *B25,* 5863. (e) Bakonyi, I.; Panissod, P.; Durand, J.; Hasegawa, R. *J. Non-Cryst. Solids* **1984,** *61/62,* 1189.

0897-4756/92/2804-0538$03.00/0