

# Composition and Microstructure of Chemically Vapor-Deposited Boron Nitride, Aluminum Nitride, and Boron Nitride + Aluminum Nitride Composites

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**The composition and microstructure of dispersed-phase ceramic composites containing BN and AlN as well as BN and AlN single-phase ceramics prepared by chemical vapor deposition have been characterized using X-ray diffraction, scanning electron microscopy, electron microprobe, and transmission electron microscopy techniques. Under certain processing conditions, the codeposited coating microstructure consists of small single-crystal AlN fibers (whiskers) surrounded by a turbostratic BN matrix. Other processing conditions resulted in single-phase films of AlN with a fibrous structure. The compositions of the codeposits range from 2 to 50 mol% BN, 50 to 80 mol% AlN with 7% to 25% oxygen impurity as determined by electron microprobe analysis. [Key words: chemical vapor deposition, aluminum nitride, boron nitride, microstructure, composites.]**

## I. Introduction

**D**ISPERSED-PHASE ceramic composites are currently being investigated as a result of the unique ability to tailor the final properties (e.g., fracture toughness, strength, corrosion resistance) by controlling the microstructure and quantity of each phase. In general, a microstructure which consists of a matrix of small equiaxed grains containing numerous uniformly dispersed small secondary particles is preferred for high-strength, high-density composites.<sup>1,2</sup>

This paper describes the use of chemical vapor deposition (CVD) to deposit single-phase coatings of BN and AlN and to codeposit coatings of BN + AlN on polycrystalline Al<sub>2</sub>O<sub>3</sub> substrates over a wide range of processing conditions. The lubricating properties of the soft, hexagonal BN combined with the high-strength, hard AlN wurtzite phase offer the promise of tailoring properties such as friction coefficient, hardness, and resistance to wear and erosion for possible radome, infrared-window, and tribological applications. The goal of this research is to characterize and to study the microstructure of BN + AlN codeposits as well as single-phase BN and AlN for different processing conditions.

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Boron nitride deposition by CVD has previously been studied extensively using several reagent systems including BCl<sub>3</sub> + NH<sub>3</sub>, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>, and B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>Cl<sub>3</sub>.<sup>3-5</sup> For low-temperature deposition (700° to 1200°C), the structure of BN is amorphous or isotropic.<sup>6</sup> BN coatings obtained at 950° to 1050°C have been shown to have a turbostratic structure as indicated by a broad (002) diffraction peak. The turbostratic structure can be viewed as a semicrystalline phase where "BN layers are stacked roughly parallel to each other but show random orientation and translation about the layer normal."<sup>7</sup> As the temperature is raised (1200° to 2100°C), the deposits are anisotropic, and the hexagonal structure becomes preferentially oriented with the basal plane parallel to the deposition surface, resulting in a sharp (002) diffraction peak. This is commonly called pyrolytic BN or PBN. The grain size of BN deposits decreases continuously from 8 to 1.5 nm as temperature is decreased from 2000° to 1200°C.

Aluminum nitride has been deposited using mainly the AlCl<sub>3</sub> + NH<sub>3</sub> reagent system. The deposition morphology varied from a hexagonal/pyramidal growth<sup>8</sup> to a columnar or fibrous growth<sup>9</sup> depending on the process conditions. Polycrystalline films have been grown from 700° to 1400°C with a preferred orientation of the (002) plane parallel to the substrate. The grain size for AlN deposits is typically 50 to 100 nm in diameter.<sup>10</sup> Several other authors have presented results for AlN, BN, Si<sub>3</sub>N<sub>4</sub>, and SiC codeposits.<sup>11-15</sup>

## II. Experimental Procedure

The CVD system used in these experiments is illustrated in Fig. 1. The films were prepared using an impinging jet geometry; details of the system and its operation have been presented elsewhere.<sup>16</sup> Aluminum trichloride, which is vaporized and transported by an argon carrier gas, and boron trichloride were reacted with ammonia. The boron source used was BCl<sub>3</sub>; several of the experiments were carried out using excess argon or hydrogen. Phase analysis of coated substrates used an X-ray diffractometer<sup>†</sup> equipped with CuK $\alpha$  radiation and operated at 40 kV. The SEM work was performed<sup>\*\*</sup> following coating of the samples with a thin layer of carbon or Au/Pd to reduce the charging of the insulating BN and AlN phases.

Plan view transmission electron microscopy (TEM) specimens were prepared by mechanical thinning to 75  $\mu$ m, dimpling, and ion beam milling using 6-kV argon ions from the substrate side only in order to preserve the coating for TEM examination. Cross-section samples were also prepared by gluing two coatings face-to-face and subsequently cutting slices from this sandwich. The cross-section specimens were

<sup>†</sup>Philips 1800.

<sup>\*\*</sup>150 Stereoscan, Cambridge Instruments Ltd., Cambridge, UK.

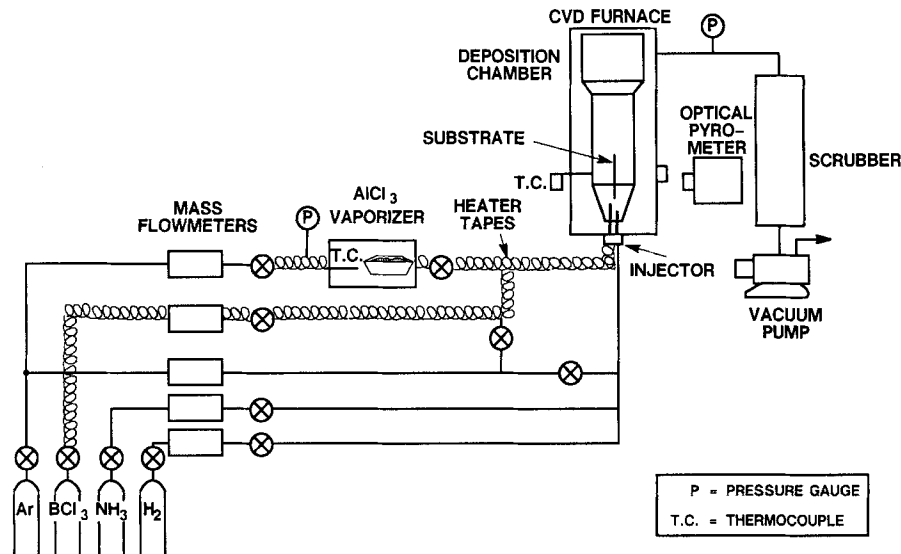


Fig. 1. Schematic diagram of CVD system used to prepare BN + AlN composites and single-phase BN and AlN films.

prepared in a manner similar to the plan view samples. Each sample was examined in a transmission electron microscope<sup>††</sup> operated at 200 kV. High-resolution images were recorded in a microscope<sup>‡‡</sup> operated at 400 kV. All photographs were taken near Scherzer defocus ( $-50$  nm) and a convergence angle of 1 mrad.

The processing conditions for the single-phase and two-phase coatings which were subsequently characterized by TEM are presented in Table I. Bulk quantitative compositions of the coatings were determined using a microprobe.<sup>§§</sup> The microprobe was operated at 10 kV with spot sizes of 1 and 10  $\mu\text{m}$ . Several samples, including standards of CVD AlN, CVD BN, and a hot-pressed AlN + BN composite were analyzed in the microprobe. The Al, B, N, and O peaks were monitored to determine the coating compositions.

<sup>††</sup>JEOL 2000FX, JEOL Ltd., Tokyo, Japan.

<sup>‡‡</sup>JEOL 4000FX.

<sup>§§</sup>JEOL 733.

### III. Results and Discussion

The single-phase BN and AlN samples were prepared as standards for the microprobe analyses and for microstructural comparison with the codeposited samples. In general, the 0.1-mm-thick coatings had a creamy white to yellowish appearance. Depending on the processing conditions, the X-ray patterns indicated a range of coating compositions and orientations, from amorphous BN + hexagonal AlN with a strong (002) orientation to amorphous AlN with hexagonal, turbostratic BN. Figure 2 presents the X-ray diffraction patterns for the two single-phase films, processed under the conditions for run 1, AlN deposition (Fig. 2(b)), and run 2, BN deposition (Fig. 2(a)), in Table I, and an ideal codeposited film which contained both hexagonal AlN and hexagonal BN processed as run 3 (Fig. 2(c)). The top pattern (BN deposition) includes a broad peak centered at  $25^\circ$ , indicative of the small grain size, hexagonal, turbostratic nature of the BN structure. Figure 2(b) has been identified as hexagonal AlN, with a sharp peak at  $36^\circ$ , showing the preferred (002) orientation.

Table I. Experimental Conditions for Single-Phase and BN + AlN CVD Experiments Studied Using TEM

Run	T (°C)	P (atm)	Flow rates (sccm)					Run time (min)
			BCl <sub>3</sub>	AlCl <sub>3</sub>	NH <sub>3</sub>	H <sub>2</sub>	Ar	
1 (J-816)	900	0.2		4.5	50		940	30
2 (J-815)	1100	0.2	10		50		940	30
3 (J-615)	900	0.2	30	5.5	50	100	1840	60
4 (J-661)*	727–1127	0.2	5	25	30	50	1800	120
5 (J-746)	1127	0.2	10	5	50		1900	60
6 (J-747)	1127	0.2	10	5	50		1900	60
7 (J-738)	927	0.2	6	13.1	75	100	1900	60
8 (J-651)	900	0.04	10	10.6	50		2735	30
Run	TEM coating appearance							
1 (J-816)	Single-phase AlN; small grains, columnar							
2 (J-815)	Single-phase BN; blisterlike; featureless							
3 (J-615)	X-ray diffraction indicated turbostratic BN with (002) oriented AlN; TEM inconclusive							
4 (J-661)*	Poor coating—AlN fiber with little or no BN							
5 (J-746)	AlN fibers surrounded by turbostratic BN with large areas of amorphous BN							
6 (J-747)	AlN fibers surrounded by turbostratic BN with large areas of amorphous BN							
7 (J-738)	AlN fibers in BN matrix, no large areas of amorphous BN							
8 (J-651)	AlN fibers—presence of BN is inconclusive from TEM—X-ray indicated BN is present							

\*Temperature variation study.

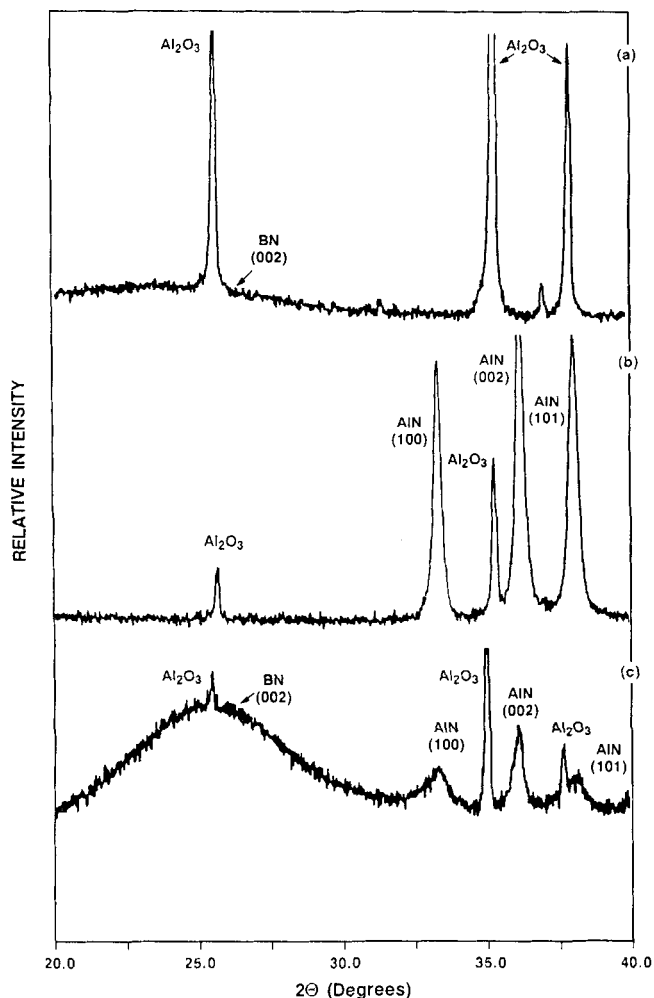


Fig. 2. XRD patterns for single-phase (a) BN, (b) AlN, and (c) codeposited BN + AlN on  $\text{Al}_2\text{O}_3$  polycrystalline substrates.

The X-ray pattern for the codeposited material (Fig. 2(c)) has both the broad BN peak and the AlN peaks.

Cross-section SEM analysis of a codeposited sample from run 4 showed a fibrous phase with a preferred orientation perpendicular to the substrate surface surrounded by a dense,

adherent matrix material, as shown in Fig. 3. A cross-section TEM image of the same sample is shown in Fig. 4. Randomly dispersed AlN fibers ( $\sim 1 \mu\text{m}$  long) were observed embedded in an amorphous-like BN matrix. Electron diffraction patterns for the two distinct phases are shown inset in Fig. 4. Other codeposited films had microstructures ranging from AlN fibers in a BN matrix with large regions of BN to only AlN fibers with little or no BN matrix phase as summarized in Table I. The AlN fibers appear to be randomly oriented in the film; however, some areas with strong preferred orientation were observed. This type of fibrous microstructure has been noted previously for codeposition of TiN fibers in a  $\text{Si}_3\text{N}_4$  matrix.<sup>15</sup> In comparison with the codeposited samples, the single-phase AlN (run 1) had a mixture of small grains with some columnar-like features as shown in Fig. 5. The single-phase BN (run 2) sample appeared blisterlike and featureless.

High-resolution TEM was used to determine the structure of the BN matrix. As shown in Fig. 6, the BN structure for samples prepared with conditions from runs 3, 5, and 6 is graphite-like and turbostratic in nature, with an interplanar spacing of  $3.33 \text{ \AA}$ . This microstructure is similar to previously reported high-density pyrolytic carbon deposits.<sup>17</sup> For the most part, the BN existed as isolated phases for processing conditions summarized in run 5; however, the BN was observed surrounding elongated AlN grains, as shown in Fig. 7. The nominal AlN fiber diameter is  $0.1 \mu\text{m}$ .

The film composition was estimated using the electron microprobe and using the single-phase coatings as standards. Oxygen as an impurity in the coatings was first observed by energy dispersive spectroscopy and was attributed to either reaction with the substrate, impurities in the  $\text{AlCl}_3$  reagent powder, or air leaks in the CVD furnace. Leak rate tests repeatedly indicated that air leaks were not the major contributor. The microprobe results indicated a range of compositions between 2–50% BN + 50–80% AlN with 7–25 atom% O in the coatings. The oxygen bonding information has not been determined; no oxygen-containing compound was identified using X-ray or electron diffraction.

#### IV. Conclusions

The characterization of AlN and BN single-phase and codeposited thin films has been accomplished using a variety of techniques. A unique microstructure consisting of AlN fibers  $0.1$  to  $1 \mu\text{m}$  long,  $\sim 0.1 \mu\text{m}$  in diameter, in a dense turbostratic hexagonal BN matrix was observed in certain coatings, which differs from the single-phase film morphologies. Elec-

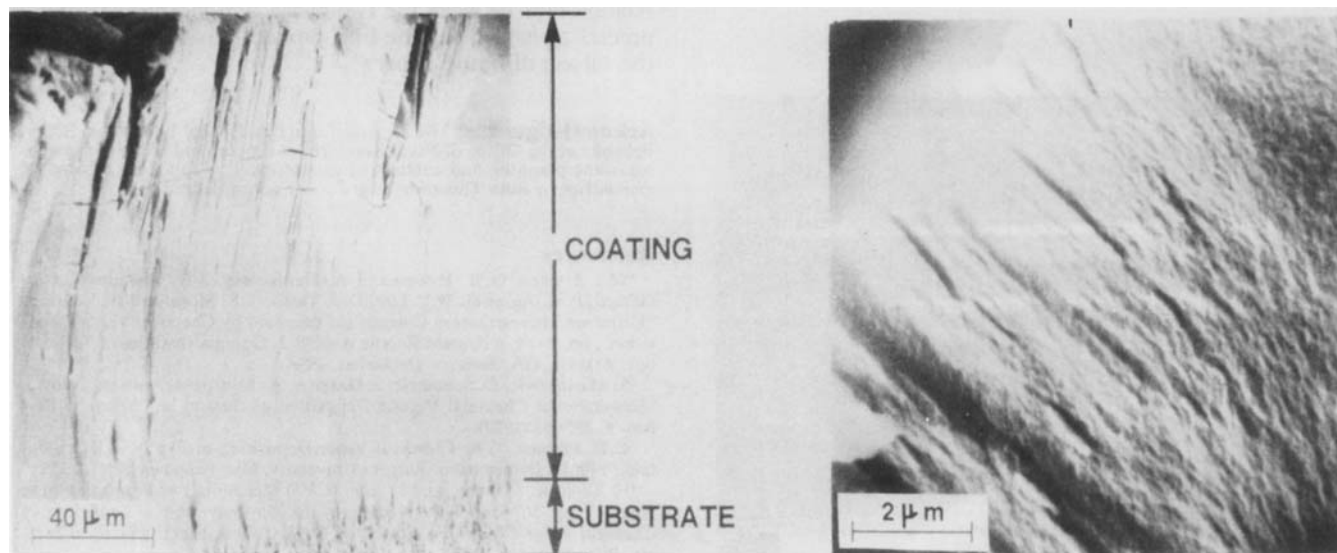
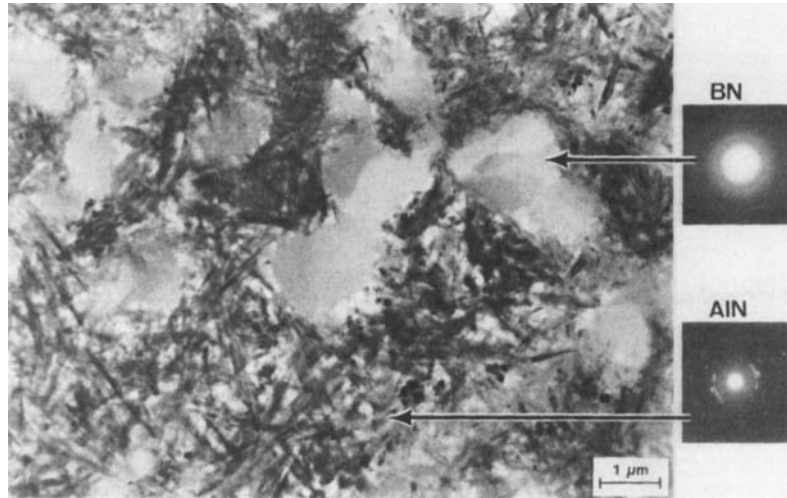
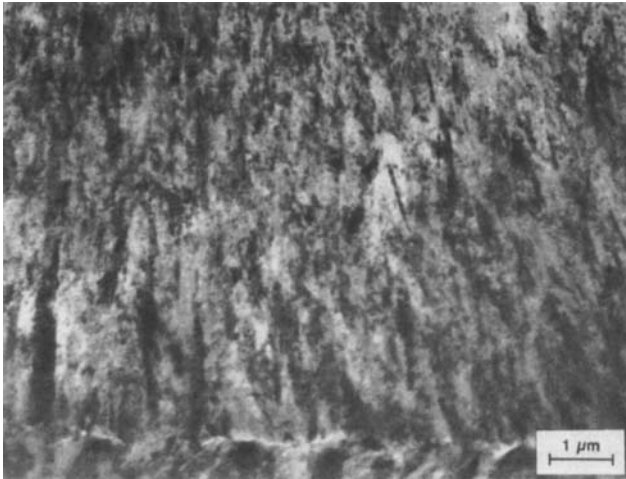


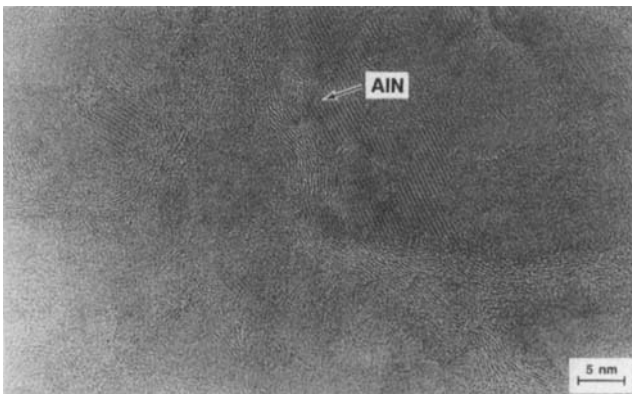
Fig. 3. SEM micrographs of composites containing turbostratic BN and anisotropic AlN.



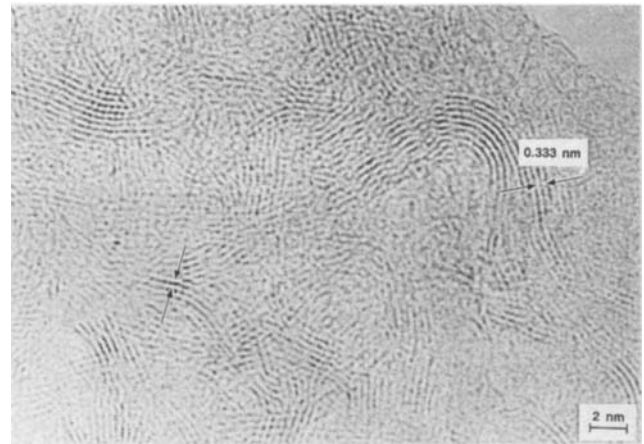
**Fig. 4.** Cross-section TEM image of codeposited BN + AlN film. Electron diffraction patterns for the two phases were used to identify the BN and AlN regions.



**Fig. 5.** Microstructure of single-phase AlN film consists of small grains with some columnar appearance.



**Fig. 6.** Turbostratic BN matrix having a lattice spacing of 0.333 nm.



**Fig. 7.** High-resolution TEM image of turbostratic BN surrounding elongated AlN grains.

tron microprobe analysis indicated the two-phase film composition ranging from 2% to 50% BN + 50% to 80% AlN with an oxygen impurity concentration of 7% to 25%. The relationships between the two-phase film morphology and a processing model, and the final properties of the films will be the subject of future papers.

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#### References

- <sup>1</sup>W. J. Lackey, G. B. Freeman, J. A. Hanigofsky, J. R. Thompson, G. J. Gérard, P. K. Agrawal, W. Y. Lee, D. J. Twait, T. S. Moss, and A. J. Green, "Ultrafine Microstructure Composites Prepared by Chemical Vapor Deposition"; pp. 9–24 in *Annual Report A-4699-2*, Georgia Institute of Technology, Atlanta, GA, January–December, 1988.
- <sup>2</sup>S. Marinkovic, C. Suznjevic, I. Dezarov, A. Mihajlovic, and D. Cerovic, "Simultaneous Chemical Vapour Deposition of Carbon and Silicon," *Carbon*, **8**, 283–95 (1970).
- <sup>3</sup>C. E. Frahme, "The Chemical Vapor Deposition of Pyrolytic Boron Nitride"; Ph.D. Dissertation. Rutgers University, New Brunswick, NJ, 1966.
- <sup>4</sup>H. Tanji, K. Monden, and M. Ide, "CVD Mechanism of Pyrolytic Boron Nitride"; pp. 562–569 in *Proceedings of the 10th International Conference of Chemical Vapor Deposition*. Edited by G. W. Cullen. Electrochemical Society, Princeton, NJ, 1987.
- <sup>5</sup>S. Motojima, Y. Tamura, and K. Sugiyama, "Low Temperature Deposition of Hexagonal BN Films by Chemical Vapor Deposition," *Thin Solid*

*Films*, **88**, 269 (1982).

<sup>6</sup>T. Matsuda, N. Uno, H. Nakae, and T. Hirai, "Synthesis and Structure of Chemically Vapor-Deposited Boron Nitride," *J. Mater. Sci.*, **21**, 649 (1986).

<sup>7</sup>J. Thomas, N. E. Weston, and T. E. O'Conner, "Turbostratic Boron Nitride, Thermal Transformation to Ordered-Layer-Lattice Boron Nitride," *J. Am. Chem. Soc.*, **84**, 4619 (1963).

<sup>8</sup>W. M. Yim, E. J. Stofko, P. J. Zanzucchi, J. I. Pankove, M. Ettenberg, and S. L. Gilbert, "Epitaxially Grown AlN and Its Optical Band Gap," *J. Appl. Phys.*, **44**, 292 (1973).

<sup>9</sup>L. V. Interrante, W. Lee, M. McConnell, N. Lewis, and E. Hall, "Preparation and Properties of Aluminum Nitride Films Using an Organometallic Precursor," *J. Electrochem. Soc.*, **136**, 472 (1989).

<sup>10</sup>M. Morita, N. Uesugi, S. Isogai, K. Tsubouchi, and N. Mikoshiba, "Epitaxial Growth of Aluminum Nitride on Sapphire Using Metalorganic Chemical Vapor Deposition," *Jpn. J. Appl. Phys.*, **20**, 17 (1981).

<sup>11</sup>D. P. Stinton and W. J. Lackey, "Simultaneous Chemical Vapor Deposition of SiC-Dispersed Phase Composites," *Ceram. Eng. Sci. Proc.*, **6** [7-8] 707-13 (1985).

<sup>12</sup>S. Zirinsky and E. A. Irene, "Selective Studies of Chemical Vapor-

Deposited Aluminum Nitride-Silicon Nitride Mixture Films," *J. Electrochem. Soc.*, **125**, 305 (1978).

<sup>13</sup>W. J. Lackey, A. W. Smith, D. M. Dillard, and D. J. Twait, "Codeposition of Dispersed Phase Ceramic Composites"; pp. 1008-27 in *Proceedings of the Tenth International Conference on Chemical Vapor Deposition*. Edited by G. W. Cullen and J. M. Blocher, Jr. Electrochemical Society, Princeton, NJ, 1987.

<sup>14</sup>T. Hirai, T. Goto, and T. Sakai, "Preparation of Si<sub>3</sub>N<sub>4</sub>-BN Composites by Chemical Vapor Deposition"; pp. 347-58 in *Materials Science Research*, Vol. 17. Edited by R. F. Davis *et al.* Plenum Press, New York, 1984.

<sup>15</sup>T. Hirai and S. Hayashi, "Preparation and Some Properties of Chemically Vapor-Deposited Si<sub>3</sub>N<sub>4</sub>-TiN Composite," *J. Mater. Sci.*, **17**, 1320-28 (1982).

<sup>16</sup>W. Y. Lee, W. J. Lackey, G. B. Freeman, P. K. Agrawal, and D. J. Twait, "Preparation and Characterization of Dispersed Phase Ceramic Composites Containing BN and AlN by Chemical Vapor Deposition," *J. Am. Ceram. Soc.*, in review.

<sup>17</sup>J. Kaee, "The Mechanism of the Deposition of Pyrolytic Carbons," *Carbon*, **23** [6] 665-73 (1985). □