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Polymeric Cyanoborane, $(CNBH_2)_n$: Single Source for Chemical Vapor Deposition of Boron Nitride Films

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Polymeric cyanoborane, $(CNBH_2)_n$, is a material readily prepared by passing hydrogen chloride through an ether suspension of sodium cyanotrihydroborate. This polymeric material was volatilized in a CVD reactor to produce, at 600°C, amorphous films containing boron, nitrogen, and carbon. Residual carbon present in the films was removed by ammonia treatment at 800°C, producing nearly stoichiometric boron nitride films that were adherent to a variety of substrates including silicon. [Key words: chemical vapor deposition, films, boranes, polymers, ammonia.]

I. Introduction

BORON NITRIDE is a compound of increasing importance for a variety of technological applications that take advantage of some of the properties of this material,[1] such as its chemical inertness, high melting point, low density, high resistivity, high thermal conductivity, and, in the case of the cubic form, an exceptional hardness. Additional applications, particularly in electronic devices, have been found for this material when applied as a thin film such as protective coatings, dielectric layers, diffusion sources, heat dissipation coatings, passivation layers, etc. Boron nitride films are deposited, as described in a recent review,[2] on a variety of substrates by CVD, PECVD, sputtering, electron beam evaporation, and ion beam deposition. Independent sources of a boron-containing species and a nitrogen-containing species are required for most of these depositions. The preparation of stoichiometric BN films requires close control of the ratio of reactant gases introduced into the deposition zone of the reactor.

The present study was prompted by the observation of adherent films on the hot walls of an apparatus used in the vacuum pyrolysis of polymeric cyanoborane, $(CNBH_2)_n$, which was found to evaporate without significant residue at 800°C. These results suggested that cyanoborane might be a convenient single source for the deposition of BN films.

II. Experimental Procedure

Polymeric cyanoborane, $(CNBH_2)_n$, was prepared according to Ref. 3. The procedure involves passing a stream of hydrogen chloride through a suspension of sodium cyanotrihydroborate, $NaBH_3CN$, in ethyl ether. The resulting sodium chloride byproduct is filtered and the solvent evaporated to isolate the product. The preparation was conducted a few times using 50 to 90 mmol of $NaBH_3CN$ in 150 mL of dry Et_2O. **CAUTION**: Recent reports[4,5] warn of possible explosions involving polymeric cyanoborane. In one instance,[4] a delayed explosion occurred after scraping the product from the walls of a glass container; furthermore, faint cracking noises were audible upon grinding small amounts in a mortar. It appears that these observations are related to the method of preparation, which, in the case of Ref. 4, involved the use of dimethyl sulfide as a solvent. Attempts to detonate small amounts of the products isolated in the course of our work failed to produce any decomposition either by scraping or by shock with a heavy object. An additional preparation in which the filtration step to eliminate sodium chloride byproduct was omitted proved to be simpler. The product from this preparation was a free-flowing powder that was equally effective in producing similar coatings as the pure cyanoborane. The presence of the salt might reduce even further any potential explosion hazard.

The polymeric cyanoborane prepared in the course of our work was characterized by its chemical analysis, infrared spectrum, and the mass spectrum of volatile members of the oligomer mixture. These properties coincided with those previously reported for this material.[3]

Film deposition was conducted in a simple CVD apparatus consisting of a quartz tube, 38-mm o.d. and 50-cm length, sealed at one end. A small test tube (10 × 75 mm) containing 100 to 200 mg of polymeric cyanoborane was placed at the bottom of the quartz tube. Specimens to be coated were placed in a support 25 cm from the bottom. The reactor was sealed and subjected to dynamic vacuum through a sidearm. The middle section of the quartz tube was surrounded by a shell furnace 15 cm in length, while the bottom section was inserted in a jacket heated with flexible heating tape. A typical deposition would be conducted by heating the specimen to 600°C while holding the bottom section at room temperature. At that point the source was heated to 150°C over a 2-h period, and then the whole assembly cooled to room temperature. The coated specimen was retrieved and weighed in an inert gas glove box. Some specimens were reloaded into a quartz tube and subjected to a stream of ammonia while heating to 800°C, holding for 2 h, and cooling to room temperature.

Characterization of the films included direct chemical analyses. Carbon was determined* on coated silicon wafers. The entire wafer was subjected to analysis. Uncoated wafers were also analyzed to establish a blank value. Boron was analyzed by ICP after stripping the coating in boiling HNO_3–H_2O_2. Infrared spectra of the crude coating and the ammonia-treated film were obtained from deposits on either CaF_2 or silicon. Attempts were also made to obtain Raman

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*Carbon analyzer, LECO Corp., St. Joseph, MI.

spectra of the films. X-ray diffraction data at a grazing angle were obtained on a coated silicon wafer. Examination of the film by TEM was performed on a specimen removed from a sapphire window with 5% HF. Additional characterization by means of XPS, Auger, and SEM was performed on silicon wafers coated with the crude and treated films. XPS spectra were obtained[†] using Al*Kα* radiation at 250 W. The C 1*s* peak at 284.6 eV was used to reference the reported binding energies. Auger spectra were obtained[‡] with a 3-keV primary electron (a 10-nA current) impinged at 55° with respect to the surface normal. These conditions were chosen because of the high degree of charging potential observed with these specimens. Resistance measurements[§] were performed on sapphire-coated specimens in an inert atmosphere using indium foil to ensure good contact on the leads. Hardness and bulk modulus were derived from measurements using a microindenter[¶], which is described in Ref. 6.

III. Results and Discussion

(1) *Chemical Analyses*

Carbon analyses of coated wafers showed that the films contained 18.5 and 2.8 wt% C for the crude and ammonia-treated films, respectively. To establish whether the decrease in carbon content was due to the ammonia or the thermal treatment, a wafer was coated at 600°C and then heated under vacuum at 800°C. The treated film contained 18.7 wt% C, thus demonstrating that the ammonia treatment caused the elimination of carbon. An additional interesting observation is that consistently the weight losses of ammonia-treated coatings were about 18%, thus showing that the ammonia treatment specifically removed carbon. Presumably the 2.8 wt% residual carbon in the ammonia-treated wafer may be reduced further by longer treatment periods. The ability of ammonia to remove carbon from ceramic materials such as Si_3N_4 or BN has been previously utilized[7,8] as a processing step.

Boron analyses showed 36 and 38.6 wt% for two independently prepared crude coatings, while that of an ammonia-treated film showed 40.4 wt%. The theoretical value for pure boron nitride is 43.5 wt%. Composition as a function of depth, as revealed by Auger spectroscopy (to be discussed in a different section), showed no oxygen other than surface contamination. The nitrogen content was calculated by difference after establishing the concentration of the other elements. These analyses revealed that the crude coating has a composition that corresponds approximately to CB_2N_2 while that of the ammonia-treated film approaches closely stoichiometric boron nitride.

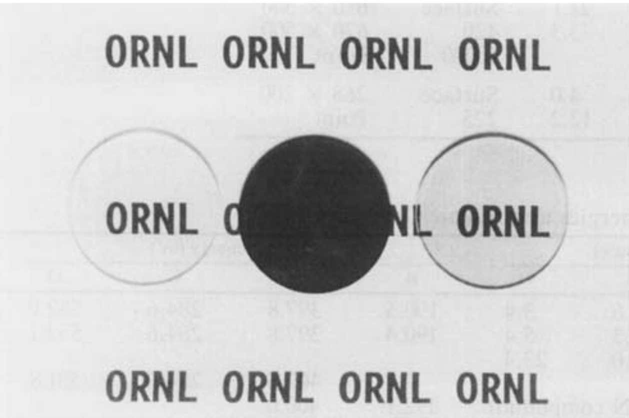

Fig. 1. Sapphire windows: uncoated, crude film, and ammonia-treated film.

The effect of the ammonia treatment on the crude film is apparent to the naked eye. Transmitted light increased dramatically after treatment. This is illustrated in Fig. 1.

(2) *Vibrational Spectroscopy*

There are numerous references to the IR spectrum of boron nitride, and these are collected in Ref. 2. The spectrum is characterized by two bands appearing at 1400 and 800 cm^{-1}. The first is assigned to BN stretching motions while the lower-energy one is attributed to BNB bending. The IR spectrum of boron nitride is not sensitive to variations in composition or crystalline form. Amorphous, hexagonal, and cubic polymorphs as well as films with variable B/N ratios have similar spectra. We find that spectra collected in the course of our work conform with the above broad generalization. However, we also found a dramatic change in the intensity and width of the stretching band upon removal of the carbon from the film as a result of the ammonia treatment. This effect is illustrated in Fig. 2, which shows the spectra of a film deposited on silicon before and after ammonia treatment. The intensity of the broader spectrum, as displayed, has been computer enhanced by a factor of 4.4 for an easier comparison. The shoulder observed in the broader spectrum at about 1580 cm^{-1} is apparently due to carbon; an additional band, also due to carbon, at 1360 cm^{-1} is covered by the BN band. The assignment of these bands to carbon is based on observations of spectra of carbonaceous materials[9] and is consistent with the disappearance of these bands upon carbon removal. The absence of any CH, NH, or BH vibrations in the spectra of the 600° or 800°C treated films apparently reflects the lack of a significant amount of hydrogen in the source material as compared with materials deposited in flow reactors with high ratios of NH_3 to B_2H_6.

Attempts to obtain a Raman spectrum of the film, which could have assisted in distinguishing hexagonal from cubic BN,[10] failed because of the interference of excessive fluorescence. Apparently this phenomenon is caused by the residual carbon in the film.[11]

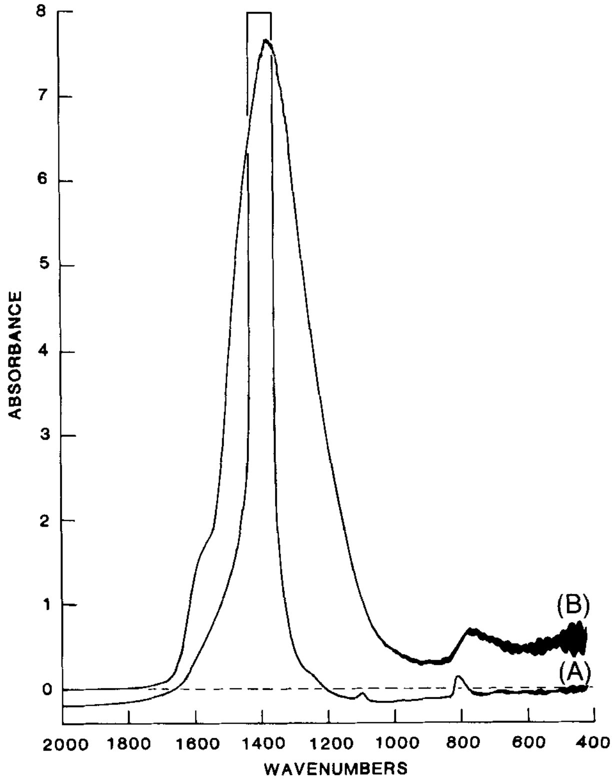

Fig. 2. Infrared spectra of (A) ammonia-treated film and (B) crude film.

[†] ESCA spectrometer, McPherson, Acton, MA.

[‡] PHI 660 scanning Auger microprobe, Perkin-Elmer, Eden Prairie, MN.

[§] Model 9520 Tera ohmeter, Guildline Instruments, Smiths Falls, Ontario, Canada.

[¶] Nanoindenter, Knoxville, TN.

(3) Microstructure

Attempts were made to establish whether the film was crystalline and to identify the polymorph present. X-ray diffraction studies on a coated silicon wafer, taken at a grazing angle, showed only a broad absorption due to amorphous material. Transmission electron microscopy conducted on a film that had been removed from the substrate and subsequently subjected to ion milling showed no diffraction pattern, and thus confirmed the XRD observation concerning the amorphous nature of the film. TEM revealed no features on the film even at a 85000× magnification.

The microstructure of coated silicon wafers, either single crystal or multigrain, as revealed by SEM at a 1000× magnification is identical with that of uncoated specimens; thus, it is apparent that, at the applied thickness of about 1 μm, the film conforms very well to the surface of the substrate.

(4) Electrical Conductivity

Attempts were made to determine, by a four-probe technique, the resistivity of films deposited on sapphire windows; however, this could not be done because of the extremely high resistance of the coatings. Direct resistance measurements were performed on the crude and ammonia-treated coated specimens using an instrument designed for measuring high resistances. The resistances measured at a 3-mm lead separation were on the order of 10^{15} Ω for both the crude and treated films.

(5) Auger and XPS

The results of the Auger and XPS analyses are given in Tables I and II, respectively. An authentic sample of bulk boron nitride was also analyzed to derive a boron sensitivity factor closely related to the samples examined. A sputter depth profile of the crude film is shown in Fig. 3. The profile reveals a relatively high oxygen concentration at the surface. This element is sputtered away very quickly while the nitrogen, carbon, and boron concentrations remain constant through the thickness of the film, which was established to be about 1 μm. The actual thickness calculated on the basis of sputtering efficiencies of Ta_2O_5 was 10600 Å. Breakthrough to the substrate is clearly revealed by the silicon signal. A sputter depth profile could not be obtained from the ammonia-treated film because of excessive interference of charging effects. Survey spectra obtained by XPS are shown in Fig. 4. The spectra are slightly shifted from each other to allow a simpler comparison. The resemblance between the BN standard and the ammonia-treated film is obvious. Closer examination at a higher resolution for each specific element revealed a coincidence in peak position as well as width. On the other hand, the crude film shows broader B and N peaks. An expanded view of the nitrogen peak is given in Fig. 5, which shows components with higher binding energies. A very similar profile is observed in the boron peak. These signals were deconvoluted and the resulting values are included in Table II. It is seen that a portion of the boron and nitrogen in the film is already constituted as boron nitride. Final conversion of the remaining nitrogen and boron into boron nitride apparently takes place as a result of the ammonia treatment.

Discrepancies between the chemical analysis and compositions derived by XPS and AES are due to the fact that the spectroscopic techniques are localized either in depth or in area and are sensitive to surface contaminations.

(6) Hardness

Establishing the mechanical properties of the ammonia-treated film was important for the characterization of this coating since the material proved to be amorphous. The measured hardness was found to be approximately 0.86 GPa, which corresponds to a Knoop hardness of about 88. This value is closer to that of hot isostatically pressed BN, 29, than that of cubic BN (in the 1000 to 3000 range) according to Refs. 1 and 2, respectively. The measured bulk modulus was approximately 6 GPa.

(7) Pyrolytic Process

The pyrolysis of polymeric cyanoborane proceeds with the production of small amounts of hydrogen cyanide, about 0.07 mmol/(mmol of starting material). This product was measured and identified by IR after being trapped downstream from the CVD reactor. Methane was also detected as a byproduct of the pyrolysis by an on-line mass analyzer attached to the vacuum line. It is significant that no boron-containing species are evolved in the pyrolysis.

IV. Conclusions

Polymeric cyanoborane provides a convenient single source material for the chemical vapor deposition of boron nitride on a variety of substrates. Although not unique as a single source precursor (borazine, its halogenated derivatives, and amine boranes have been used in the past), the simplicity in prepara-

Table I. Experimental Auger Atomic Concentrations

	Composition from multiplexed spectra (atom%)					
Sample	B	N	C	O	Sample analysis depth (Å)	Area (μm)
BN standard	34.9	35.8	27.2	2.1	Surface	670 × 500
	45.7	42.0	12.6		Surface	Point
Crude film	18.8	11.2	48.9	21.1	Surface	670 × 500
	34.3	21.2	41.3	3.3	420	670 × 500
	35.0	23.5	35.0		10000	Point
NH_3 treated	33.5	39.6	23.0	4.0	Surface	268 × 200
	38.2	36.3	13.3	12.2	225	Point

Table II. XPS Experimental Binding Energies and Atomic Concentrations

	Composition (atom%)				Binding energy (eV)			
Sample	B	N	C	O	B	N	C	O
BN standard	47.4	43.1	5.8	3.4	190.5	397.8	284.6	532.0
BN film—NH_3 treated	40.1	37.2	17.3	5.4	190.4	397.8	284.6	532.1
BN film—not treated (components)	25.4*	15.2†	36.0	23.4				
		0.8				402.5	284.6	531.8
	17.1	5.0	(B–N compound)		192.1	400.0		
	8.2	9.3	(BN)		190.2	398.0		

*Two boron species deconvoluted. †Three nitrogen species deconvoluted.

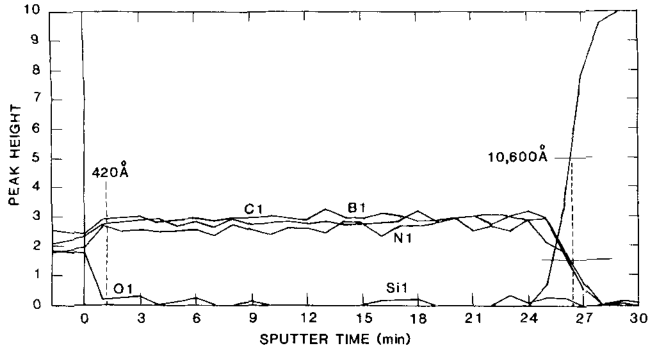

Fig. 3. Sputter depth profile of crude film.

tion and handling, as well as the composition of the coating, makes polymeric cyanoborane an attractive source for the deposition of boron nitride films.

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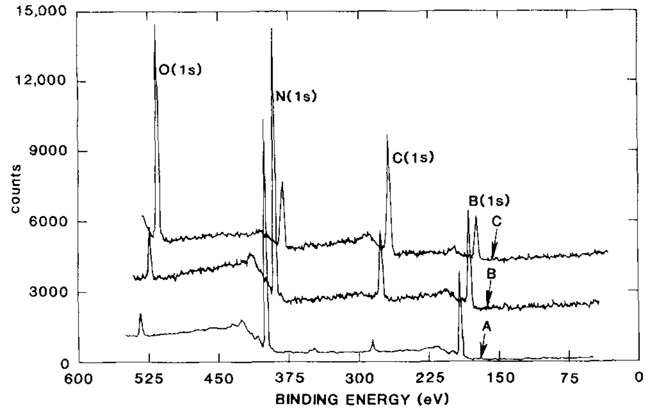

Fig. 4. XPS survey spectra of (A) BN standard, (B) ammonia-treated film, and (C) crude film.

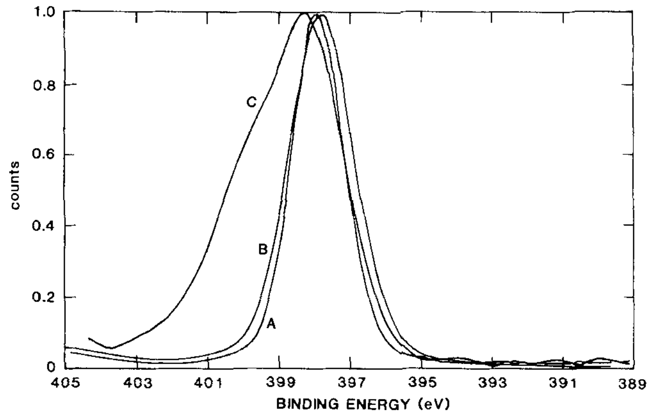

Fig. 5. XPS nitrogen 1*s* peak of (A) BN standard, (B) ammonia-treated film, and (C) crude film.

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