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TECHNICAL REPORT ECOM-01343-1

CHEMICAL VAPOR DEPOSITED MATERIALS FOR ELECTRON TUBES

PROGRESS REPORT

by

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October 1965

ECOM

UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.

Contract DA 28-043-AMC-01343(E)
RAYTHEON COMPANY
Waltham, Massachusetts

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S-803

Technical Report ECOM-01343-1 October, 1965

CHEMICAL VAPOR DEPOSITED MATERIALS FOR ELECTRON TUBES

Report No. 1
1st Quarterly Report
15 May 1965 to 14 August 1965
Contract No. DA 28-043-AMC-01343(E)
DA Project No. 1P6-22001-A-005-01-11

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SUMMARY

This program was established to investigate chemical vapor deposition as a method of producing materials or coatings for use in vacuum electron devices.

Experiments have been conducted with two methods of producing CVD BN, one resulting in a product with isotropic properties, the other with anisotropic properties. Depositions have been made at temperatures ranging from 1350°C up to 1900°C. BN deposits one-quarter inch and more have been obtained on the interior of a 2 in. × 2 in. × 10 in. graphite box. Experiments were made with various surface finishes of the substrate. Our results indicate that, by following the same general priciples which have been developed for pyrolytic graphite, anisotropic BN can be formed after some experimentation into any specific shape whose thickness is not greater than 10 percent of its radius of curvature.

Several properties of isotropic CVD BN have been measured. Preliminary measurements of its thermal conductivity show it to be about equivalent to nickel, and its thermal expansion nearly matches that of tungsten. The modulus of elasticity is low, and the coefficient of thermal expansion is low, consistent with a high thermal shock resistance. Flexural strengths average about 10,000 psi. X-ray examination showed no preferred orientation. No helium permeation was obtained, and degassing studies demonstrated good vacuum properties at least to 1000°C.

Some experiments have been conducted with CVD silicon nitride and zirconium diboride. CVD TiB_2 has a secondary emission ratio of 0.6.

A work function of 2.2 eV has been measured for CVD ZrC with a $\langle 110 \rangle$ orientation.

FOREWORD

This program was authorized by the U. S. Army Electronics Command under DA Project No. 1P6-22001-A-055-01 for the conduct of research investigations in accordance with Technical Guidelines TT-26 dated 10 April 1964, entitled "Research on Chemical Vapor Deposited Materials for Electron Tubes." The objective of the program include:

a. The investigation of chemical vapor deposition as a method of producing materials and coatings for general use and/or specific application in electron devices,

b. The determination and control of the process variables in CVD and their relationship to the development of new or improved characteristics in materials, compounds, and coatings for electron devices, and

c. The measurement of the pertinent chemical, physical, electrical, and mechanical properties associated with the specific and most promising areas of utilization of the produced CVD materials.

The authors wish to thank Mr. S. Cvikevich for making the x-ray evaluations, Mr. R. Donadio for measuring the mechanical properties, and Mr. H. Schilling for assisting with the thermal conductivity and thermionic emission measurements reported here.

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I. INTRODUCTION

Present day electron tubes possess many advantages over their solid-state counterparts. They have higher power capabilities, possess more consistent characteristics from device to device, and appear to be more resistant to radiation damage than the equivalent solid-state devices. In display, storage, and image tubes, rapid and easy switching or scanning is possible due to the ease of deflection of the electron beam. In many cases tubes possess a higher frequency capability, operate over a broader bandwidth, operate into a higher input and output impedance, and introduce a smaller coupling between input and output circuits than do their solid-state counterparts.

Electron tubes do suffer from limitations in size, reliability, power consumption, and cost. These limitations could be at least partially overcome if proper materials were available to the tube designer. It is the purpose of this program to investigate chemical vapor deposition as a method of producing materials or coatings for use in electron devices, with the ultimate goal of solving some of the materials problems of the tube designer.

II. THE CVD PROCESS

The chemical vapor deposition (CVD) process has many advantages over more conventional techniques for preparing materials. Probably the most important of these is that the resultant material is very pure and dense. In addition, highly oriented deposits can be formed whose properties are often similar to those of a single crystal of the same substance, although the material can be made in much larger sizes. Large sheets and other shapes can be fabricated, either as a coating or as a deposit, in thicknesses ranging from several hundred angstroms up to a few centimeters. CVD processes can be used to form the most refractory substances at temperatures far below their melting or decomposition points, and at temperatures at which their vapor pressures are negligible. The properties of CVD materials can be significantly and controllably altered by the co-deposition of alloying atoms. Depending upon the concentration of the alloying atoms, either solid solutions or two-phase substances can be formed. Either substitutional or interstitial solid solutions can be deposited depending upon the nature of the alloying atoms. Composites made up of alternating layers of two or more different materials can be prepared by cycling the composition of the vapors from which the materials are deposited.

CVD consists essentially of reacting volatile compounds (of the elements composing the material to be deposited) at a surface which is heated to a temperature at which the compounds decompose or react to form an adherent coating. The by-products of the reaction can be pumped off, flushed off in a stream of carrier gas, or removed by combination with a mass of some suitable reactive material in the system. Most vapor depositions are carried out at pressures of the order of one-hundredth of an atmosphere or so, although much higher or lower pressures can be employed.

Although the CVD process is conceptually simple, it is actually quite complicated. A complete characterization of the process requires a knowledge of the rate constants of all reactions involved, diffusion coefficients, thermal conductivities and accommodation coefficients for all gaseous species, flow velocities, substrate temperatures and temperature gradients through the gases, pressure and pressure gradients, geometry, vapor compositions, and their variation temporally and spatially. These many variables are obviously difficult to fix in a practical system. Past experience has shown that specification of the substrate temperature, the vapor composition, the linear flow velocity, the pressure, the system geometry, the deposition rate, and the substrate surface produce deposits with reproducible properties.

III. CVD INSULATING MATERIALS

A. Introduction

If a material could be fabricated which was simultaneously a good electrical insulator and a good thermal conductor, and it was otherwise suitable for use in a vacuum electron device, it would find many uses within tubes. Particular applications might include collector and control electrode supports, and microwave circuit supports. If the material was sufficiently refractory and chemically unreactive it could also be used very advantageously as a spacer between cathode and heater. Although BeO has been used for some of these applications, it is hazardous to handle. In addition, its thermal conductivity diminishes to low values as the temperature increases so that at a few hundred degrees centigrade it has lost much of its usefulness. CVD boron nitride (BN) and Si_3N_4 appear to be more promising in this regard. CVD BN has a relatively high thermal conductivity (about one-quarter that of copper) even at 1000°C, and has good dielectric properties to at least 1500°C. We are exploring both CVD BN and Si_3N_4 as possible vacuum tube materials.

B. Boron Nitride

1. General

Although BN has many properties which would make it attractive for use in electron devices it has not been used to any extent in tubes. This is principally because the hot-pressed shapes which have been tried up to now are hygroscopic, and after a time show poor vacuum, mechanical, and electrical properties. This degradation has been attributed to the impurities, such as boric oxide, which are introduced in order to form the material by conventional means.

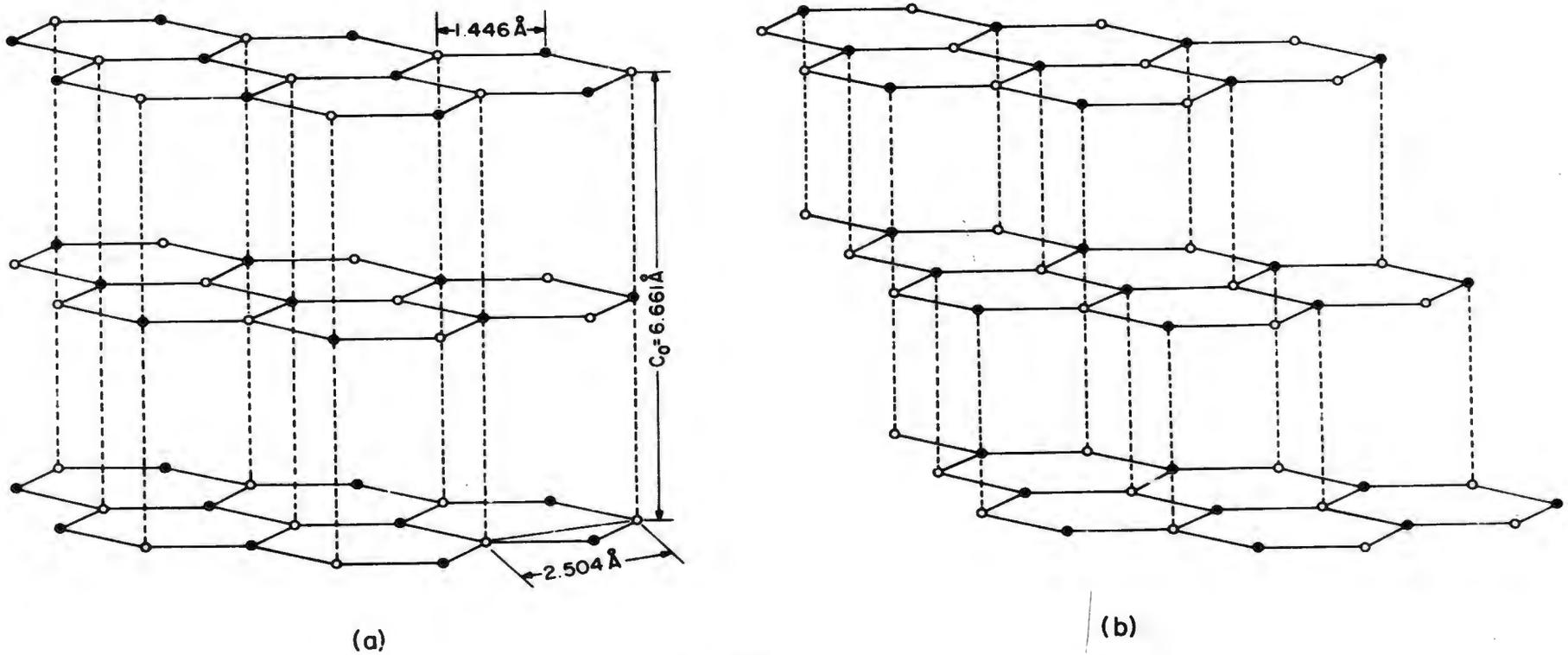
The production of shapes by the CVD technique overcomes this objection. A very pure product is obtained which avoids most of the drawbacks of the hot-pressed boron nitride.

The most common structural form of BN is the hexagonal form, although two other allotropic forms are known to exist. Rhombohedral BN has been reported to co-exist with hexagonal BN when it is prepared by the fusion of sodium borate and potassium cyanide.[1] Cubic BN is made by a high pressure technique similar to that used in making synthetic diamonds.[2]

Hexagonal BN is isostructural with graphite; in fact it is commonly referred to as white graphite. BN consists of hexagonal rings arranged in a two dimensional network and stacked one on top of the other (Fig. 1). Each ring is composed of alternating boron and nitrogen atoms with a bond length of 1.446Å. The networks are stacked so that each atom of boron has nitrogen atoms above and below and vice versa for each nitrogen atom. The distance between each second layer, its "c" spacing, is 6.6612Å for the hexagonal form,[3] 3.615Å for the cubic form,[2] and 10.01Å for the rhombohedral form.[1]

Structurally, CVD BN is similar to CVD graphite; that is, order exists within the sheets but the stacking of the individual sheets is random.

Although BN is referred to as a new material, it was prepared as a powder as early as 1842 by Balmain who reacted boric acid with mercuric cyanide and sulphur and also boric acid with potassium cyanide.[4,5] In spite of the relative ease with which BN powder can be produced, it remained a laboratory curiosity until recently because of the difficulty in forming it into useful shapes.



(a) Hexagonal Structure **(b) Rhombohedral Layer Structure**

Boron Nitride

Figure 1

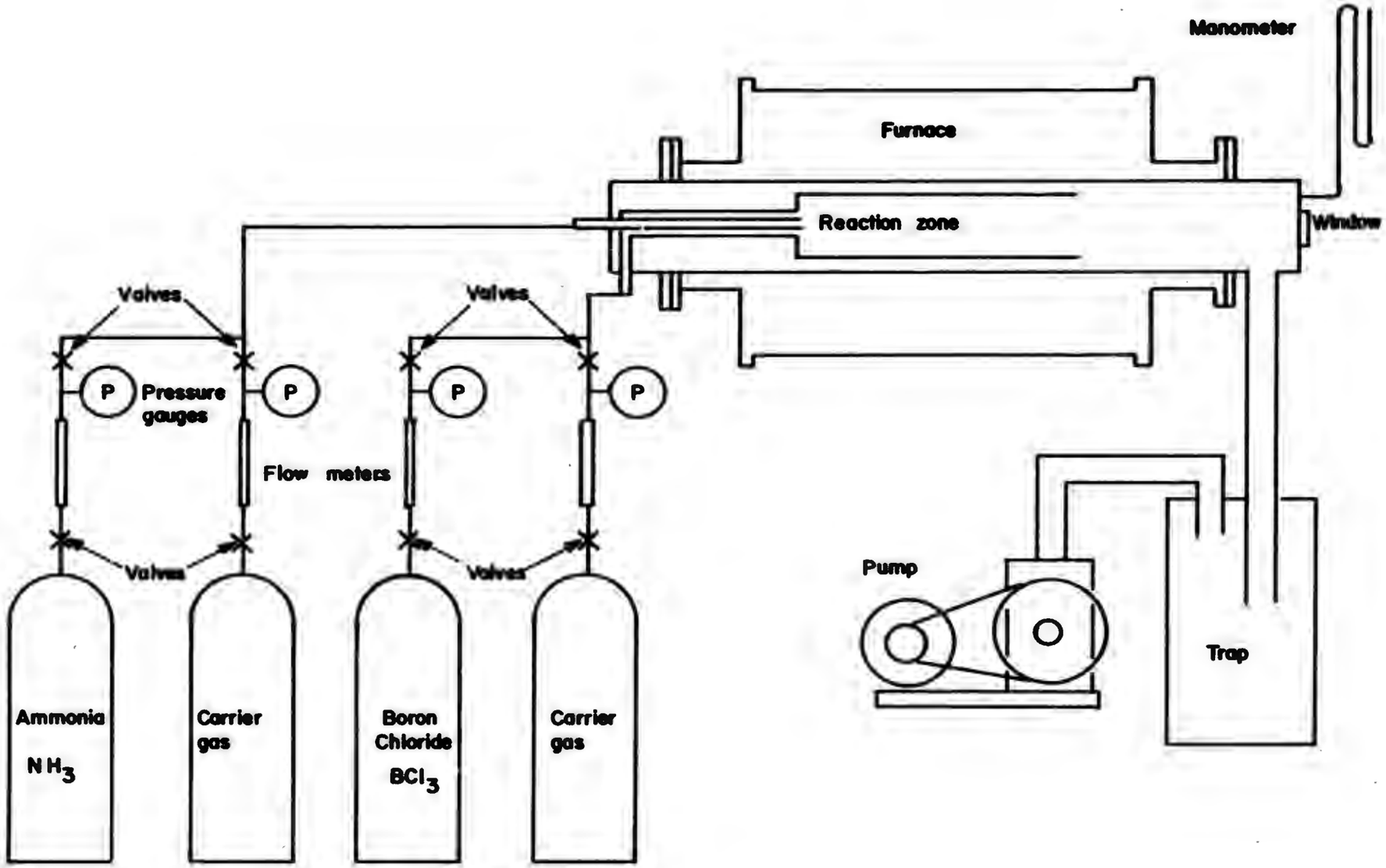
About a decade ago it was found commercially feasible to prepare BN by the hot-pressing technique. Gilpin[6] has described a commercial process for making hot-pressed BN from boric oxide and ammonia. The hot-pressing method, however, requires the addition of a binder and a fluxing agent and as a result impurities, deleterious to the material properties, are incorporated in the final shape.

2. Deposition Process Runs

During this quarter we have experimented with two ways of producing BN by the CVD technique. The first method uses BCl_3 (boiling point 12.5°C) and NH_3 as source materials with unreactive gases as carriers. Figure 2 shows schematically the set-up used. The source gases (plus carrier gases) are directed onto a hot substrate (1000° - 2000°C) and they react to deposit BN.. The unreacted gases and the gaseous reaction products are removed by a cold trap and a mechanical pump. This process ordinarily results in a dense, highly oriented deposit with anisotropic properties. In the remainder of this report the material produced by this process will be referred to as anisotropic BN and the process itself as the chloride process.

The properties of CVD BN are related to the source materials and the processing technique employed. Thus, it should be possible to produce material with a wide range of values for any specific property. However, this also implies that the process must be closely controlled if reproducible material is to be attained.

Some calculations have been made in an effort to gain a better understanding of various steps of the BCl_3 CVD process for preparing BN. The ammonia surviving a pass through a process furnace at various temperatures and flow rates has been estimated semi-quantitatively.



Boron Nitride Deposition System

Figure 2

Results indicate no ammonia survival at temperatures greater than 1200°C under the various flows comparable to those used in the process runs. As might be expected, with decreasing temperatures and increased flows more ammonia survives. It has been observed that significant quantities of NH_4Cl are found condensed in the pump side of the furnace system at deposition temperatures as high as 1900°C, and larger quantities at 1700°C. Ammonium chloride was thought to be formed from HCl, the by-product of the nit. ide formation reaction, and unreacted NH_3. However, it has been shown that unreacted NH_3 cannot survive. Therefore, the nitrogen found in the NH_4Cl must survive the furnace, without changing valence, in some stabilized form such as NH_2BCl_2 or some similar fragment of incompletely formed nitride.

Calculations were also made to determine how fast gases introduced into the hot ambient heat up. Several simplifications were assumed, one of them being that no water-cooled gas inlet was used. Under the conditions usually used in a process run it was found that gas near the center of the tube may pass through the furnace without being heated to much over 350°C. Gas near the edge of the tube naturally heats up to near tube temperature.

We have made some attempts to determine the effect of deposition temperature upon the properties of anisotropic BN formed by the boron chloride process. In general, CVD BN formed at a low deposition temperature (1000°C) is glassy, hard, and has a yellow-brown cast. Material made above 1500°C is opaque, white, and somewhat softer. Translucency seems to increase with a decrease in process temperature. Most of our work has been done at the higher temperatures (1600–1900°C) because at these temperatures the deposition rates are high enough to be useful. The differences in properties observed to date may be related as

much to the deposition rate as to the deposition temperature. The density of the deposit does appear to be greater at the higher deposition temperatures. The crystallite size and orientation is also greater at the high temperatures.

At deposition temperatures* of 1600° and 1900°C, pressures of 6 to 12 torr, NH_3 to BCl_3 ratios of 2 to 1, BCl_3 flow rates of about 0.6 mol per hour, and deposition times of 30 to 60 hours, anisotropic BN deposits one-quarter of an inch or more in the thickest spot were obtained on the interior of a 2 in. × 2 in. × 10 in. graphite box (see Table I). When a box with a planar surface was used, the deposit tended to bow away from the substrate and form a curved surface, convex toward the interior of the box. This was probably a result of the greater lateral growth of the first deposited layers after deposition as they were held at the deposition temperature for several tens of hours as compared with the last deposited layers. Nearly planar deposits were obtained at 1900°C by using a box with concave sides with a radius of several inches so as to compensate for the differential growth of the material during deposition.

Experiments were also made with various surface finishes of the substrate. A smooth substrate seemed desirable to reduce the number and size of the nodules, and thus to reduce the incidence of delaminations. Unfortunately, the adherence of the BN to the graphite substrate was so poor with a smooth finish that "bowing" of the deposit became a serious problem. A flash coat of pyrolytic graphite over the ATJ graphite did not make the coating any more adherent. The problem was solved by laying down a flash coat of isotropic CVD BN just prior to starting the deposition from BCl_3.

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* The deposition temperatures quoted in this report were measured at one end of the substrate and may differ to some degree from the actual temperature of the substrate surface.

TABLE I

SUMMARY OF CVD PROCESS RUNS - ANISOTROPIC BORON NITRIDE

(Deposition Conditions)

Number	Temp (°C)	Time (hrs)	Average Flow Rates (mol/hr)				Pressure Average (torr)	Rates Max (mils/hr)	Density (g/cc)
			Boron Compound	Carrier Gas	NH_3	Carrier Gas			
BN-28	1600	35	0.59	1.3	1.01	6.1	6	5.2	1.76 1.85
BN-33	1700	50	0.59	1.3	0.69	6.1	6	6.0	2.10
BN-37	1700	60	0.59	1.3	0.69	6.1	6		1.98
BN-26	1900	30	0.59	1.3	1.01	6.1	6	4.8	2.12
BN-31	1900	51	0.59	1.3	1.01	6.1	6		2.18

We have occasionally had problems with sooting, which is the spontaneous nucleation of solid material in the vapor, whenever the furnace pressure exceeded some critical value. When soot deposits on the material during its growth, additional nodules are initiated, and the resulting material often shows voids, and is weak and friable. Sooting has been controlled by better control of the process variables and in particular by reducing the furnace pressure.

The flow rates of source materials and diluents for the preparation of anisotropic BN must be varied for material made at different pressures and deposition rates. Quantities of NH_4Cl are condensed on the pump side of the furnace system even at deposition temperatures of 1900°C, and in some cases long runs have had to be terminated because the furnace exhaust has become clogged with NH_4Cl. The terminations by clogging have been largely eliminated by the use of less NH_3 especially in the low temperature runs. We believe that optimum materials ratios have been determined (see Table I) for the formation of BN at the various deposition temperatures.

The thickness distribution of the CVD BN deposits are critically dependent upon the substrate geometry, as are the ingredient mixing and flow patterns. Thus far most of our experiments have been concerned with simple boxes with planar and concave sides. We have formed plates one-quarter of an inch in thickness. Although the substrate geometry is somewhat more critical for BN than for pyrolytic graphite, our results indicate that anisotropic BN can be formed into any specific shape whose thickness is not greater than ten percent of its radius of curvature, by following the same general principles that have been developed for pyrolytic graphite.

Table II shows the relationship between the density, the deposition temperature, and the deposition rate for isotropic CVD BN. The material

has a relatively low density, but does not possess interconnecting pores. As previously noted for anisotropic CVD BN, the density of the deposit appears to depend as much upon the rate of deposition as upon the deposition temperatures.

3. Properties

a. Thermal Conductivity

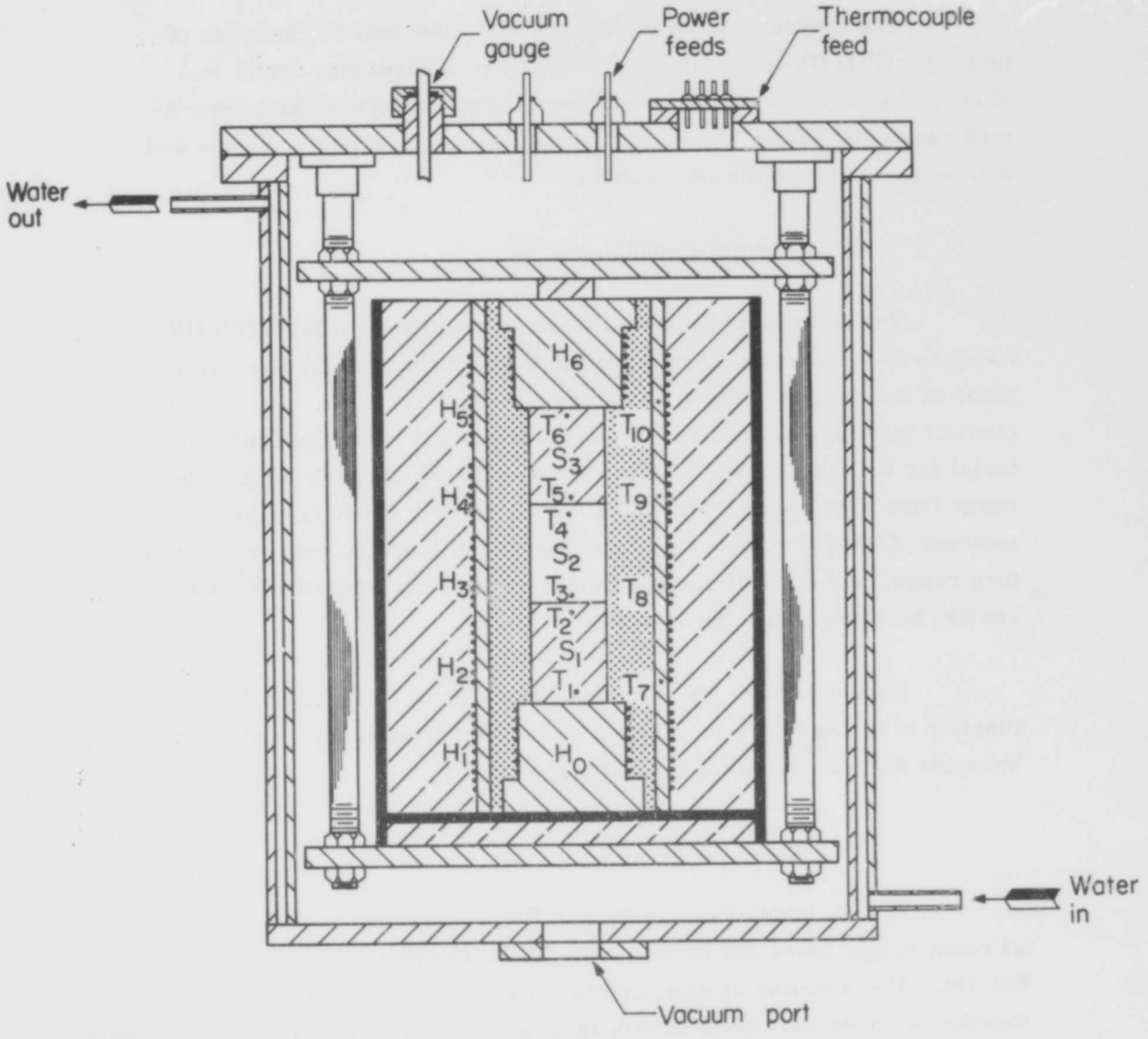
Preliminary measurements of the relative thermal conductivity of isotropic BN (samples BN-22, formed at 1500°C, and BN-30, formed at 1700°C) have been made from 200° to 800°C.

The apparatus used is shown in Fig. 3. The sample (S_2 in Fig. 3) is made approximately one inch in length and of a convenient measured thickness. Reference standards (S_1 and S_2) are made the same thickness and length as the sample. The temperature and temperature gradients of the samples and reference standards are measured by high output thermocouples T_3, T_4, T_1, T_2, T_5, and T_6. The thermal gradient across the interfaces between the standards and the sample can be found from the thermocouples T_2, T_3, and T_4, T_5. A thermal gradient is established by heaters H_0, H_1, H_2, H_3, H_4, and H_5. The heaters are adjusted to minimize the lateral heat flow as measured by thermocouples T_7, T_8, T_9, and T_{10}, thus ensuring that the same amount of heat flows through the standards and the sample. With the proper choice of standards and proper adjustment of the heaters, conductivities can be measured to an accuracy of ± ten percent.

TABLE II

THE DENSITY AND DEPOSITION RATES OF ISOTROPIC CVD BN

Number	Temp (°C)	Rate Max (mils/hr)	Density (g/cc)
BN-32	1350	1.9	1.44
BN-22	1500	2.8	1.30
BN-27	1700	5.4	1.18
BN-30	1700	6.1	1.22
BN-25	1850	5.1	1.41



Comparative Apparatus for Determining Thermal Conductivity

Figure 3

The measurements indicate that the thermal conductivity of isotropic CVD BN in the plane of deposition is about one-fourth that of copper and is relatively insensitive to temperature in the temperature range measured. More exact measurements are in progress and will be described in the next report.

b. Thermal Expansion

The thermal expansion of isotropic and anisotropic CVD BN samples were measured both parallel to and normal to the deposition plane of the sample. The results are shown in Table III. The coefficient of thermal expansion is virtually identical for the isotropic material for both directions, and is nearly constant over the temperature range from room temperature to 1000°C. The thermal expansion of isotropic CVD BN very nearly matches that of tungsten over this temperature range, and it should be possible to make a tungsten-to-BN seal quite readily by conventional techniques.

Figure 4 shows the thermal expansion of anisotropic BN as a function of temperature for the two deposition directions. It shows a behavior similar to that of pyrolytic graphite.

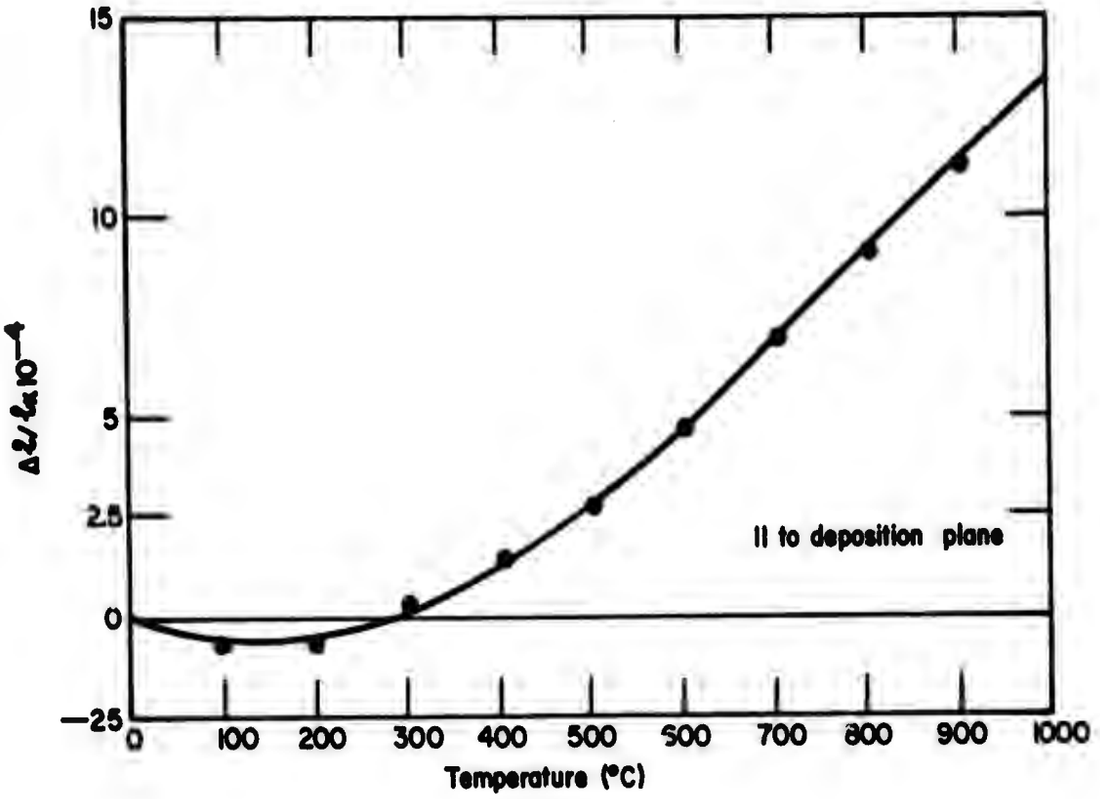
c. Elastic Constants

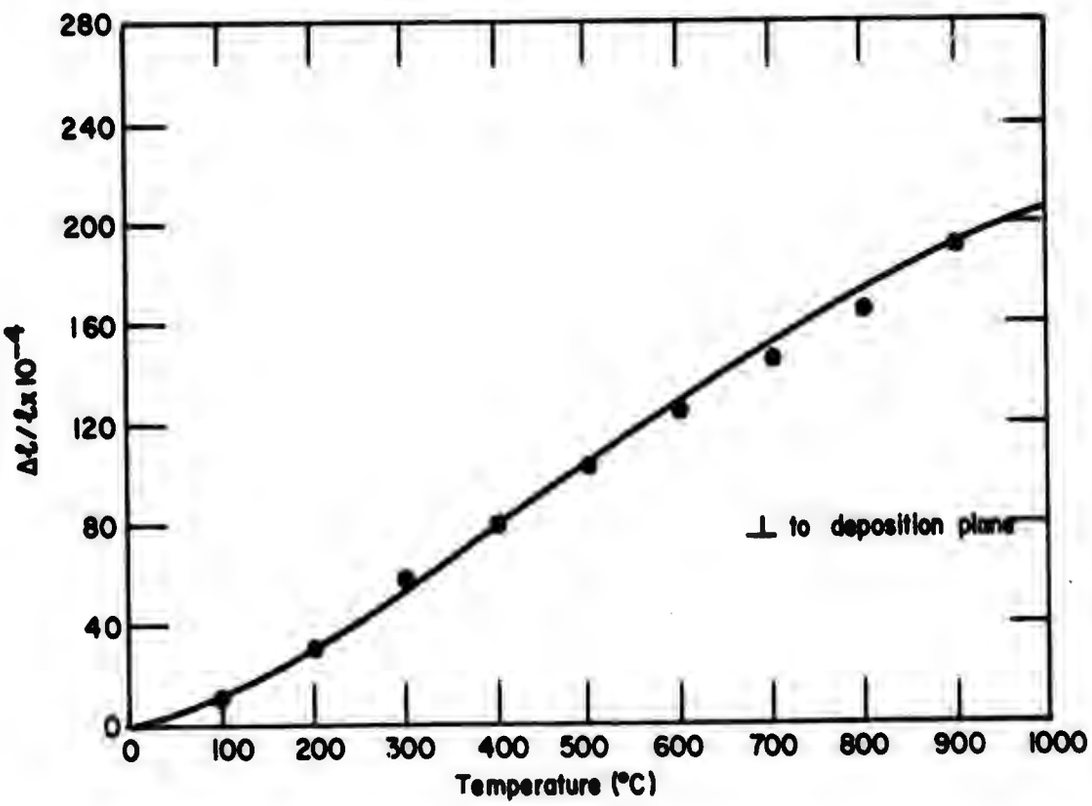
The modulus of elasticity and Poisson's ratio have been measured at room temperature for isotropic CVD BN (samples BN-32, BN-22, and BN-30). The modulus of elasticity is relatively low (see Table IV), which together with its low coefficient of thermal expansion indicates that the material should possess a high thermal shock resistance.

TABLE III

THERMAL EXPANSION OF CVD BORON NITRIDE

Sample No.	BN-32		BN-8 (like BN-22)		BN-30		BN-28	
Dep. Temp	1350°C		1500°C		1700°C		1600°C	
Process	Isotropic		Isotropic		Isotropic		Anisotropic	
Temp °C	(a) $\Delta_{\ell/\ell}$	(c) $\Delta_{\ell/\ell}$	(a) $\Delta_{\ell/\ell}$	(c) $\Delta_{\ell/\ell}$	(a) $\Delta_{\ell/\ell}$	(c) $\Delta_{\ell/\ell}$	(a) $\Delta_{\ell/\ell}$	(c) $\Delta_{\ell/\ell}$
100	0.14×10^{-3}	0.06×10^{-3}	0.15×10^{-3}	0.06×10^{-3}	0.16×10^{-3}	0.27×10^{-3}	-5.2×10^{-5}	1.07×10^{-3}
200	0.42	0.11	0.47	0.11	0.48	0.52	-6.1	3.14
300	1.29	0.17	0.91	0.17	0.92	0.79	3.7	5.73
400	2.16	1.24	1.43	0.40	1.41	1.25	15.6	8.05
500	2.99	1.71	1.96	0.82	1.86	1.75	27.5	10.25
600	3.28	2.37	2.31	1.25	2.35	2.21	48.0	12.45
700	3.49	2.84	2.68	1.68	2.81	2.65	70.6	14.66
800	3.77	3.30	2.98	2.28	3.26	3.11	93.1	16.73
900	4.07	3.77	3.28	3.05	3.72	3.59	113.6	18.98
1000	4.12	4.23	3.54	3.38	4.08	4.05	134.1	20.50
1075	4.23	4.48	3.63	---	4.45	4.29	148.7	21.55
	α_a	α_c	α_a	α_c	α_a	α_c	α_a	α_c
(0-1000) in./in./°C	4.12×10^{-6}	4.23×10^{-6}	3.54×10^{-6}	3.38×10^{-6}	4.08×10^{-6}	4.05×10^{-6}	1.34×10^{-6}	20.5×10^{-6}
α_c/α_a	1.03		0.95		0.99		15.3	





The Thermal Expansion of Anisotropic CVD BN Parallel and Perpendicular to the Deposition Plane

Figure 4

TABLE IV

MECHANICAL PROPERTIES OF BORON NITRIDE

Process Run Number	Deposition Temp (°C)	Flexural Strength				Elastic Constants	
		Sample Number	Orientation	psi $\times 10^3$ (RT)	psi $\times 10^3$ (1000°C)	E	μ
BN-32	1350	1	Parallel	11.0	4.4	4.8×10^6 psi	0.23
		2	"	10.9	3.3		
		3	"	10.0	2.8		
		Avg		10.6	3.5		
		4	Perpendicular	14.5			
		5	"	13.7			
		6	"	14.1			
		Avg		14.0			
BN-22	1500	1	Parallel	10.9	6.5	2.2×10^6 psi	0.27
		2	"	10.9	8.3		
		3	"	10.0	7.2		
		Avg		10.6	7.3		
		4	Perpendicular	12.7	4.5		
		5	"	11.7	4.6		
		6	"	11.1	6.7		
		Avg		11.8	5.3		
BN-30	1700	1	Parallel	11.5	14.2	1.6×10^6 psi	0.23
		2	"	15.0	10.6		
		3	"	14.3	13.7		
		Avg		13.6	12.8		
		4	Perpendicular	8.2	10.7		
		5	"	17.0	13.2		
		6	"	12.6	8.2		
		7	"	12.4			
		Avg	"	14.0	10.7		

d. Flexural Strength

The flexural strength of isotropic CVD BN samples has been measured at room temperature and 1000°C using a three-point loading method. The results are given in Table IV. The limited data available indicate that the high temperature flexural strengths appear to be deposition temperature dependent.

e. Chemical Resistance

BN is a remarkably inert material. Even at elevated temperatures only a few reagents attack it. In order to test its reactivity with molybdenum, a sheet of isotropic BN (sample BN-22) was given a metallographic polish and sandwiched between two sheets of molybdenum which had also been polished. The sandwich was heated in vacuum to 1700°C for two hours under a load of about 500 g/cm^2. Subsequent microscopic examination of the polished surfaces showed no apparent interaction between the BN and the molybdenum. A similar experiment conducted with an alumina body commonly used for microwave windows resulted in a marked etching of the molybdenum and a weak bonding of the molybdenum to the alumina.

To test their reactivity with water, samples of isotropic BN were weighed, boiled in distilled water, and reweighed. Both samples BN-22 and BN-30 gained a slight amount of weight after $2\frac{1}{2}$ and $5\frac{1}{2}$ hours of boiling (Table V). The reason for this behavior is not clear, and further investigations are in progress.

TABLE V

WEIGHT GAIN OF BORON NITRIDE WITH BOILING

Sample No.	Boiling Time (hrs)	Wt Before Boiling (g)	Wt After Boiling (g)	Wt Gain (g)
BN-22	2.5	0.680	0.692	0.012
BN-30	5.5	1.985	2.018	0.033

f. Microstructure

Metallographic specimens were prepared from each process run listed in Tables I and II, and were microscopically examined under polarized light at low and high magnifications. The anisotropic specimens invariably showed the typical cone structures seen in Fig. 5. In addition, delaminations between layers were occasionally observed, especially before the bowing problem was alleviated.

Specimens of isotropic CVD BN showed no observable porosity by metallographic examination, even at the highest useful magnification (1500X). There appeared an extremely fine-grained structure which was just below the limit of resolution of the instrument. Samples were given a light molten alkali etch but this did not help to resolve the structure by ordinary light microscopy.

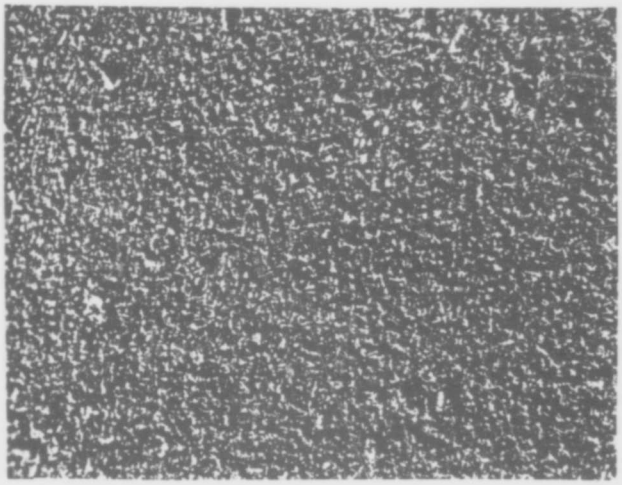
Carbon replicas were obtained, and electron micrographs made. Figure 6 shows the structure observed for sample BN-22 at a magnification of 9000X. No porosity was identified even at the highest magnification. The sample appeared to be made up of randomly oriented platelets with a fairly uniform size of about one-quarter micron. As is mentioned elsewhere, no permeation of the sample could be detected at differential pressure of one atmosphere of helium. Any pores which do exist must be very small and non-interconnecting.

g. Preferred Orientation in BN

The technique used for quantitative measurement of preferred orientation in pyrolytically deposited boron nitride (BN) is the one previously developed for measuring preferred orientation in pyrolytic graphite (PG).[7,8]

Photomicrograph of CVD Anisotropic BN (50X)

Figure 5



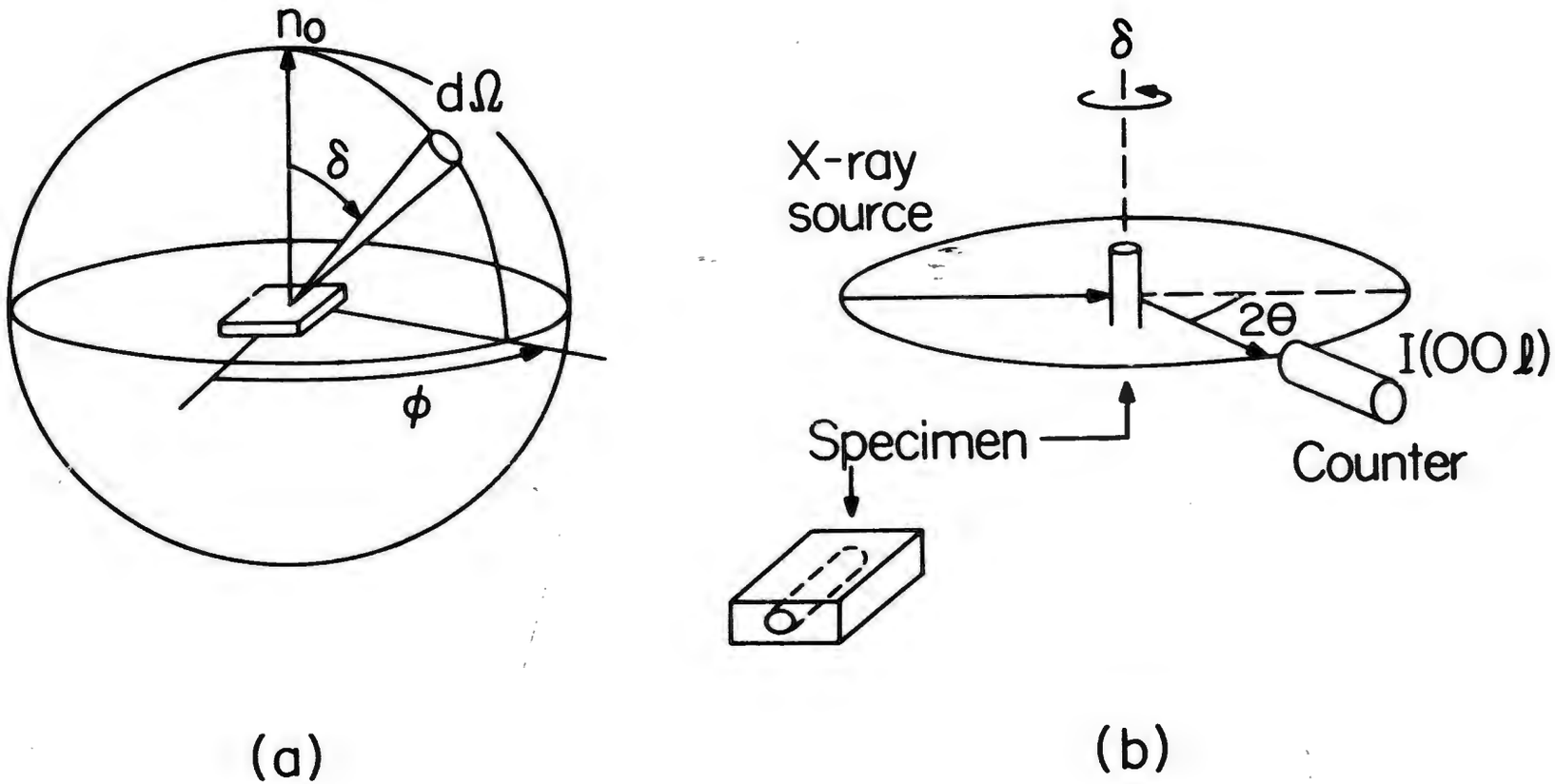
Electron Micrograph of Isotropic Boron Nitride Sample BN-22 at 9000X

Figure 6

The preferred orientation is conveniently described in terms of an orientation density, $n(\delta, \phi) = dV/d\Omega\ (\delta, \phi)$, where dV is the fraction of volume oriented such that the normals to the basal planes lie in the solid angle element $d\Omega\ (\delta, \phi)$, and δ and ϕ are the angles of inclination and azimuth shown in Fig. 7(a). A measure of this orientation density is given by the integrated intensity of a (00ℓ) reflection if the diffraction vector, $(\vec{s} - \vec{s}_o)/\lambda$, lies in the solid angle element $d\Omega\ (\delta, \phi)$. Here, $\vec{s}_o$ and $\vec{s}$ are unit vectors in the direction of the incident and scattered x-ray beam, respectively, and λ is the x-ray wavelength. The proportionality between the integrated (00ℓ) intensity and the orientation density remains constant for all possible specimen orientations relative to the diffraction vector if the absorption conditions are kept constant, e.g., if the specimen is a sphere assumed to be of uniform density. Initial measurements indicated that the orientation density is independent of ϕ as might be expected from the process of deposition. Therefore, the actual measurement of the orientation density can be limited to its δ-dependence, i.e., to the rotation about an axis parallel to the deposition plane. For this purpose rod-shaped specimens were cut and mounted as shown in Fig. 7(b).

During the measurements the counter was set at a fixed 2θ position corresponding to the 002 peak position determined for the condition when the preferred orientation axis points in the same direction as the diffraction vector. From our previous experience we know that the peak position and shape of the 002 reflection will not change significantly as a function of the angle of rotation δ. However, even if such changes were to occur, our use of an open counter (no receiving slit) would tend to minimize their effects on recorded intensity.

The angle of rotation δ was obtained by mounting the cylindrical BN specimens on a single crystal orienter. The δ rotation was motorized and the speed of the motor was synchronized with the recorder chart



Setup for Making Preferred Orientation Measurements

Figure 7

speed in such a way that the display of the δ scale in degrees would have a reasonable relation to the chart paper. In our case 10 degrees of rotation in δ were displayed as 1/2 inch of chart paper.

As was previously observed all the BN samples obtained from BCl_3 had some preferred orientation, whereas those deposited from an organic boron compound were isotropic. Heat treatment at 2000°C in a nitrogen atmosphere did not have any marked effect on the degree of preferred orientation of the BN samples obtained from either of the source materials.

Figures 8(a) and 8(b) show examples of the preferred orientation measurements obtained from the anisotropic and isotropic materials respectively. The preferred orientation data shown in Fig. 8(a) can be analyzed quantitatively by fitting an analytical function. Previous work on pyrolytic graphite suggests that the function should be of the form $K + N \cos^n \delta$,[9] where K is the isotropic part and $N \cos^n \delta$ describes the anisotropic or angularly dependent part of the preferred orientation distribution. The $\cos^n \delta$ function can be used to fit the preferred orientation distribution data for values of $0 \leq \delta \leq \pi/2$ and n any real positive number greater than 1. For intercomparison between samples with different amounts of preferred orientation the analytical function should be used in a normalized form: $K/N + \cos^n \delta$. Then the n parameter can be used to establish the relative amounts of preferred orientation in the anisotropic fraction of each material and $\frac{aK}{N}$ will give the ratio of the amount of isotropic to anisotropic material within each sample where a will be a function of n.

Figure 8(a) shows an example of how the above analytical function can be fitted to experimental data.

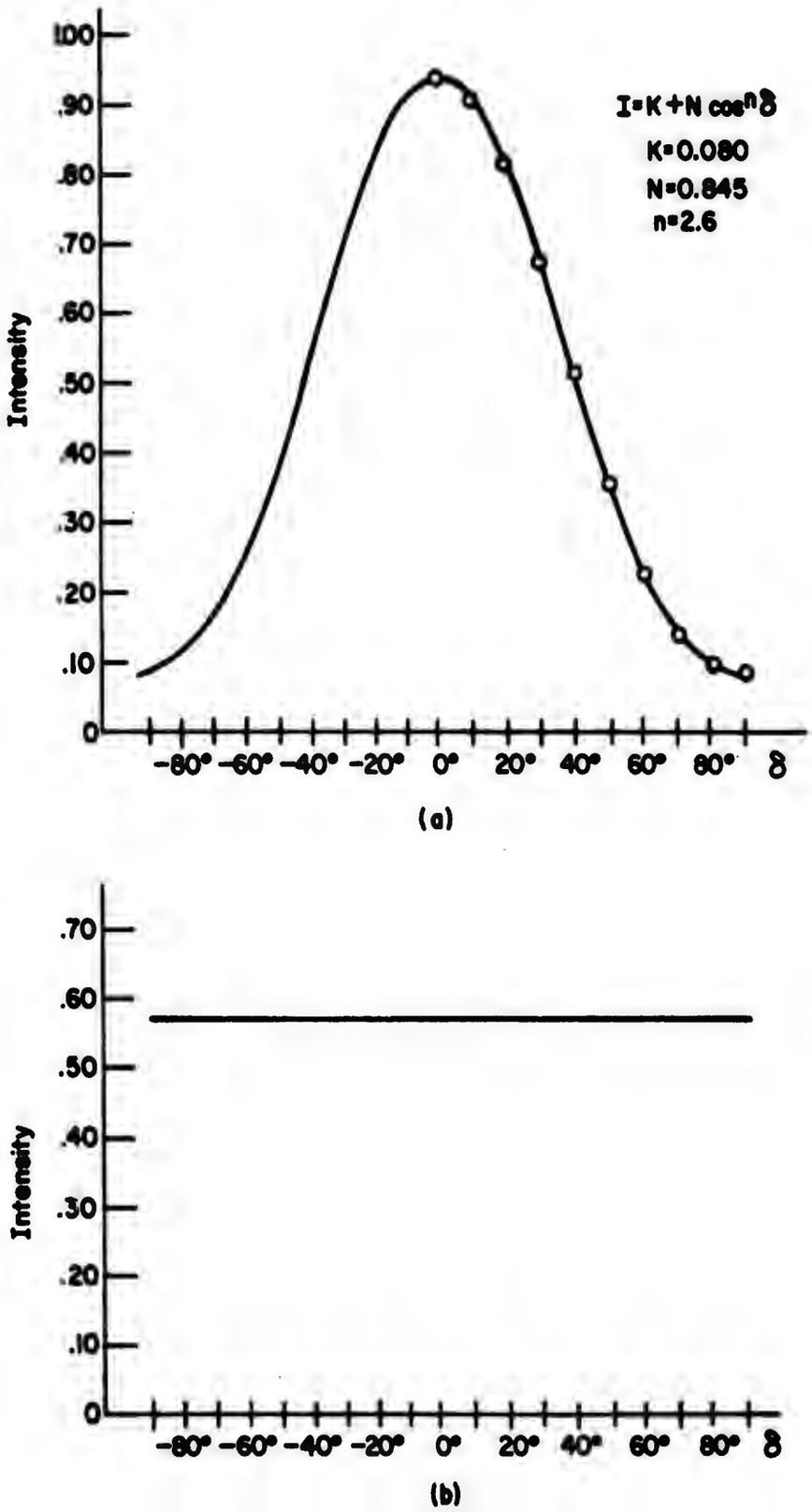


Figure 8 Preferred Orientation Data for Anisotropic and Isotropic BN Showing the Intensity of the 002 Reflection as a Function of the Angle of Sample Rotation δ

h. Degassing Properties

In order for a material to be useful in an electron tube it must have good vacuum properties. The removal of absorbed and dissolved gases from a material used in a vacuum tube usually requires that it be degassed on the pumps at some elevated temperature prior to the sealing off operation. Thus a useful material generally possesses a vapor pressure of less than 10^{-5} torr at the bake-out temperature so that it can be processed. Even more stringent requirements are placed on components, such as heaters and cathodes and their support structures, which normally operate at high temperatures in the vacuum. Any vaporization which occurs during the life of the tube, whether it leads to a gas or to a solid condensate, ordinarily causes a degradation in the characteristics of the device. In addition, materials which are to be used as part of the vacuum envelope must remain impermeable to all ambient gases and vapors for several years.

Although it is common practice to accelerate the degassing of materials by raising the temperature for some specified time period there is a scarcity of high temperature degassing data even for ordinary materials and virtually none is available for CVD materials. On the basis of low temperature data, it is possible to predict the high temperature behavior of a material if certain physical properties, such as diffusivity, permeability, solubility, the composition of evolved gases, and adsorption energies, are known. Dayton[10] has studied this problem in some detail, and has obtained equations relating the outgassing rate of solids for absorbed gases to the diffusion coefficient, the temperature, and the concentration of gas within the solid. He has derived formulas for the common case in which the bake-out cycle can be approximated by a step-function corresponding to raising the temperature suddenly from room temperature to a constant bake-out temperature and then after a time interval suddenly

lowering the temperature again by rapid cooling to room temperature. Unfortunately, factors which are not included in Dayton's model, often are important in real tubes, and consequently the application of his equations may yield results which, although they are qualitatively in agreement with experimental data, show quantitative deviations.

The apparatus shown in Figs. 9 and 10 has been set up to measure the degassing rates of CVD materials at temperatures of up to 1000°C. In this system degassing rates at temperature are calculated from the measured pressure drop across an orifice of known conductance. The apparatus consists of a quartz sample container held at each selected temperature by means of a resistively heated tube furnace surrounding it. The total pressure of the sample chamber is measured with a Bayard-Alpert type gauge tube, while the partial pressures of the component gases are determined at periodic intervals with an omegatron mass spectrometer. The entire specimen chamber is pumped through an orifice of known conductance. The system, with the exception of the ion pumps and the gas system used for calibration of the omegatron, is bakeable to 400°C.

Partial pressure measurements give valuable information as to the nature of the degassing processes in materials. Huber[11] has surveyed the present techniques for measuring partial pressure in high and ultra-high vacuum systems. For our system it was desirable to use a device which was small, bakeable, and possessed a sufficiently high sensitivity to detect partial pressure of 10^{-9} torr or less. Despite its limitations, the omegatron seemed suited for this application.

The omegatron, its characteristics and associated electronics, have been described in detail in the literature (see Huber for references), but its limitations should be mentioned. The omegatron operates on the

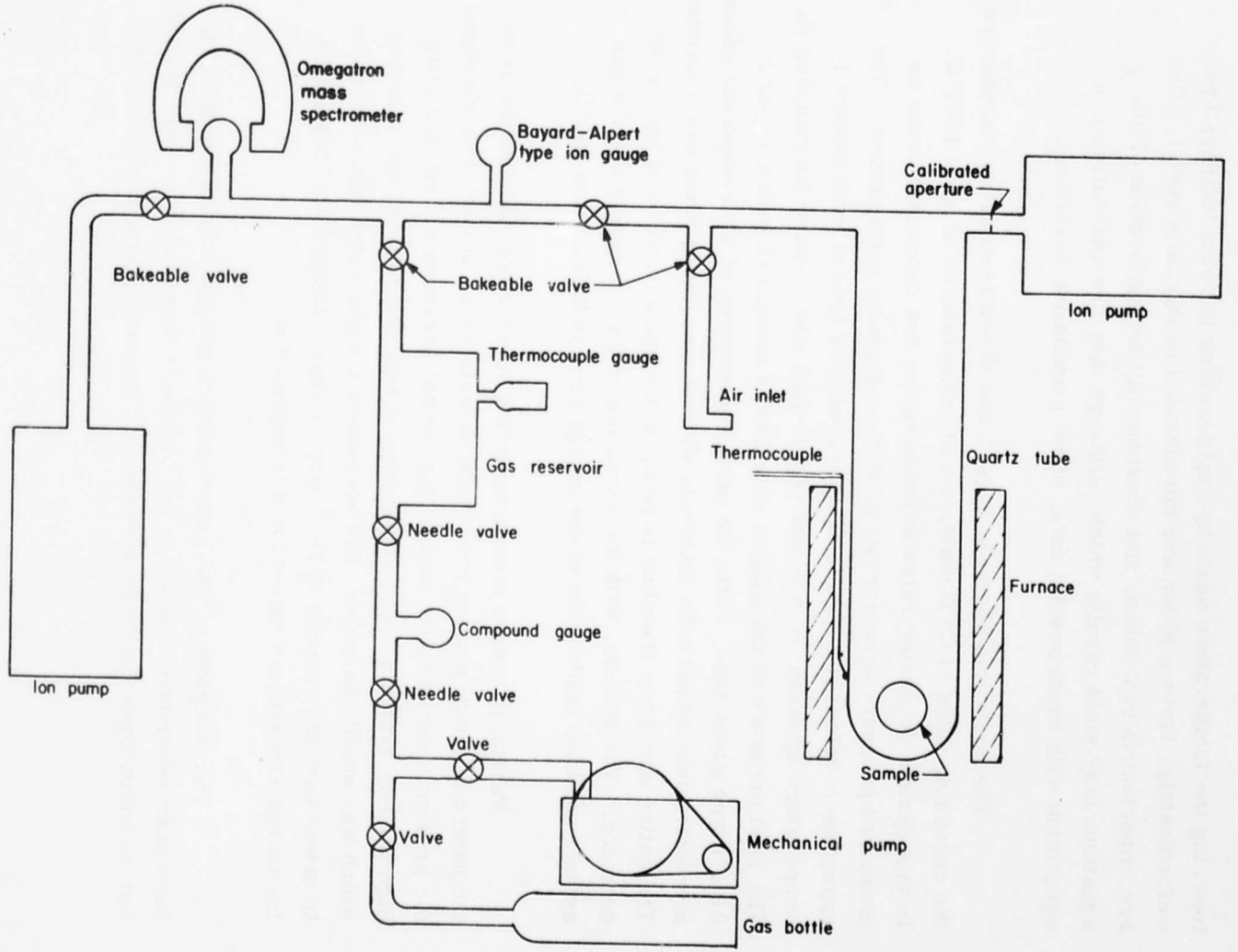
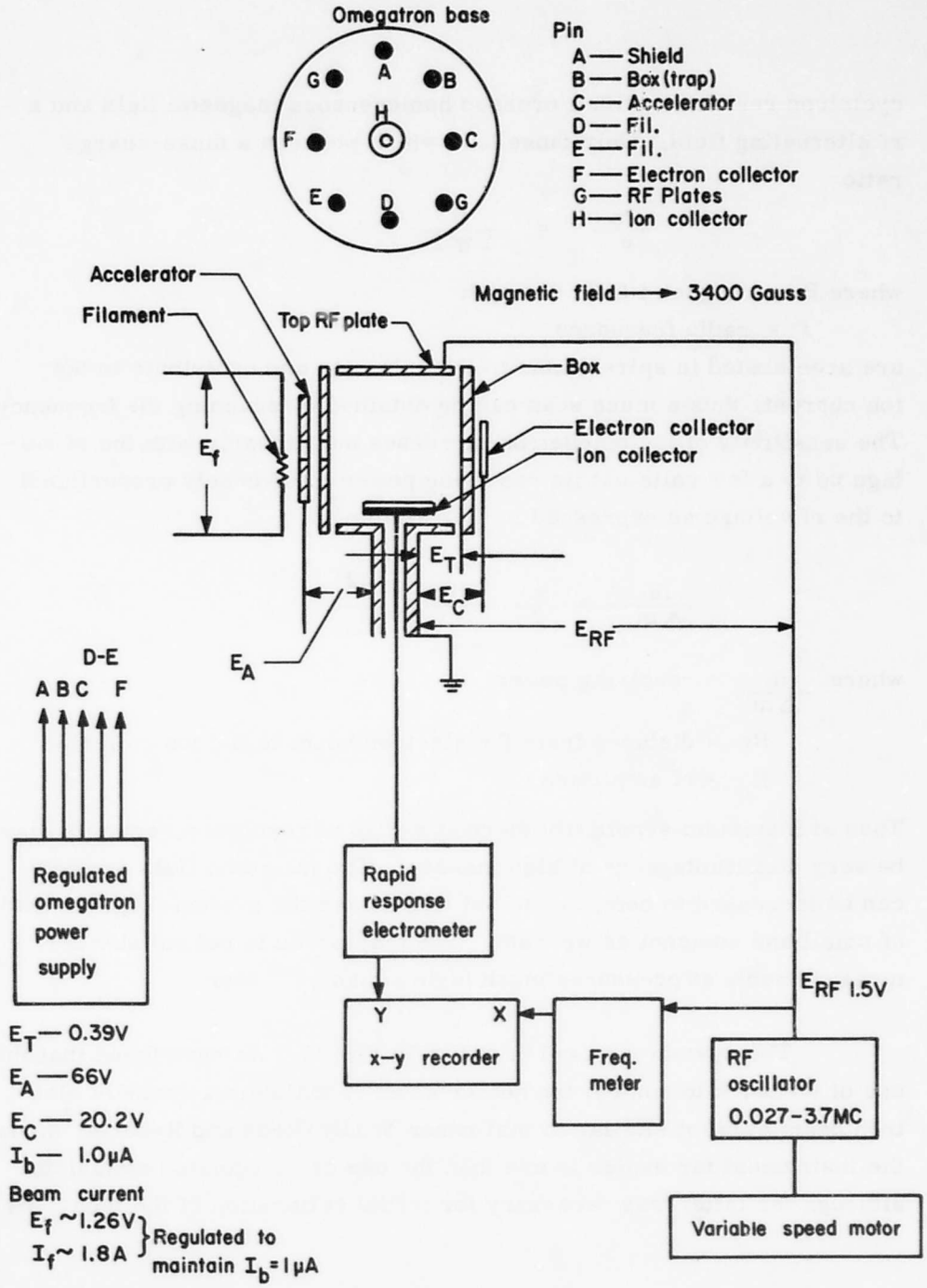


Figure 9 Degassing Analysis Setup



Omegatron Setup

Figure 10

cyclotron resonance with a crossed homogeneous magnetic field and a rf alternating field. Only those ions which possess a mass-charge ratio

$$\frac{m}{e} = \frac{B}{2\pi f}$$

where B = magnetic field strength

f = radio frequency

are accelerated in spiral paths to the collector and contribute to the ion current, thus a mass scan can be obtained by scanning the frequency. The sensitivity of the omegatron increases non-linearly with the rf voltage up to a few volts but its resolving power is inversely proportional to the rf voltage as expressed in the relation

$$\frac{m}{\Delta m} = \frac{e}{2} \quad \frac{Ro}{m} \quad \frac{B^2}{E_o} \quad .$$

where $\frac{m}{\Delta m}$ = resolving power

Ro = distance from the electron beam to the ion collector

E_o = rf amplitude.

Thus at maximum sensitivity there is a loss of resolution, and this may be very disadvantageous at high masses. The magnetic field strength can be increased to compensate but this makes the system large instead of small and compact as we want. The omegatron is not suitable for measurements at pressures much higher than 10^{-5} torr.

The system we used is shown in Fig. 10. We have found that the use of feedback to control the heater so as to maintain a constant electron beam current similar to that described by Giedd and Roberts[12] made the instrument far easier to use than the use of unregulated emission, although the latter was necessary for initial calibration of the tube. We

also recorded the ion collector current as a function of frequency using a sensitive electrometer to drive the y-axis of an x-y recorder, and a frequency meter to drive the x-axis. In this way the speed of the motor, which varies the frequency of the rf oscillator, was not critical so long as it was not too fast for the response time of the electrometer. Since the mass-charge ratio for a given magnetic field is inversely proportional to frequency, our recording amounted to the use of mass as the x-axis, and could be very conveniently superimposed for comparison regardless of the scanning rate.

The voltages which give the best results vary from tube to tube even if they are made according to the same design. For these experiments we used the following conditions:

E Accelerator	=	66 volts dc
E Electron Collector	=	20.2 volts dc
E Trapping	=	0.39 volts dc
E_{rf}	=	1.5 volts RMS
i electron	=	1.0 microamps
B	$\cong$	3400 gauss

For calibration, gases were leaked into the omegatron from a reservoir at reduced pressure with the omegatron valved off from the specimen chamber through a bakeable valve. A second ion pump was provided to keep the omegatron under vacuum when the valve to the specimen chamber is closed. Calibration runs were made for nitrogen, ammonia, helium, and oxygen.

The background outgassing rates from the system and the quartz sample tube must be subtracted from the total outgassing measured during

outgassing tests on the sample. For this reason before each run the empty system was pumped down and baked out at about 400°C for several hours. During the bakeout the ion gauge was outgassed. An ultimate pressure in the 10^{-9} torr at room temperature range was usually obtained. The quartz sample tube was then heated gradually to 1100°C and the partial pressure, and the total pressure in the system was periodically recorded. With the empty sample tube at 1100°C combined outgassing and permeation rate was ordinarily about 10^{-9} torr liters/sec./cm^2. The system was allowed to cool and again brought up to 1100°C. The outgassing rates proved to be small in comparison with the total gas loads encountered when the system was run with test samples, especially at the lower temperatures. The system after cooling was then ready to be vented with dry nitrogen and to be loaded with the sample.

Sample BN-27 (an isotropic BN formed at 1700°C), which because of its low density might be expected to have a high gas content, was selected for outgassing studies. The sample (6 cm^2 in area) was placed in the quartz sample chamber of the outgassing apparatus, which was immediately evacuated. Prior to testing, the sample had been stored in a normal laboratory atmosphere for about thirty days after deposition. The system attained a pressure of about 3×10^{-8} torr after overnight pumping at room temperature.

The procedure adopted for the outgassing studies was to raise the temperature stepwise in time. The maximum pressure attained at each temperature was noted and the sample was held at that temperature until the system pressure dropped by a factor of two; whereupon the temperature was again increased. Omegatron mass spectrometer scans were made when the temperature was attained and just prior to increasing the temperature. Temperature increments of 100°C were employed where possible. In the range between 200 and 500 degrees smaller

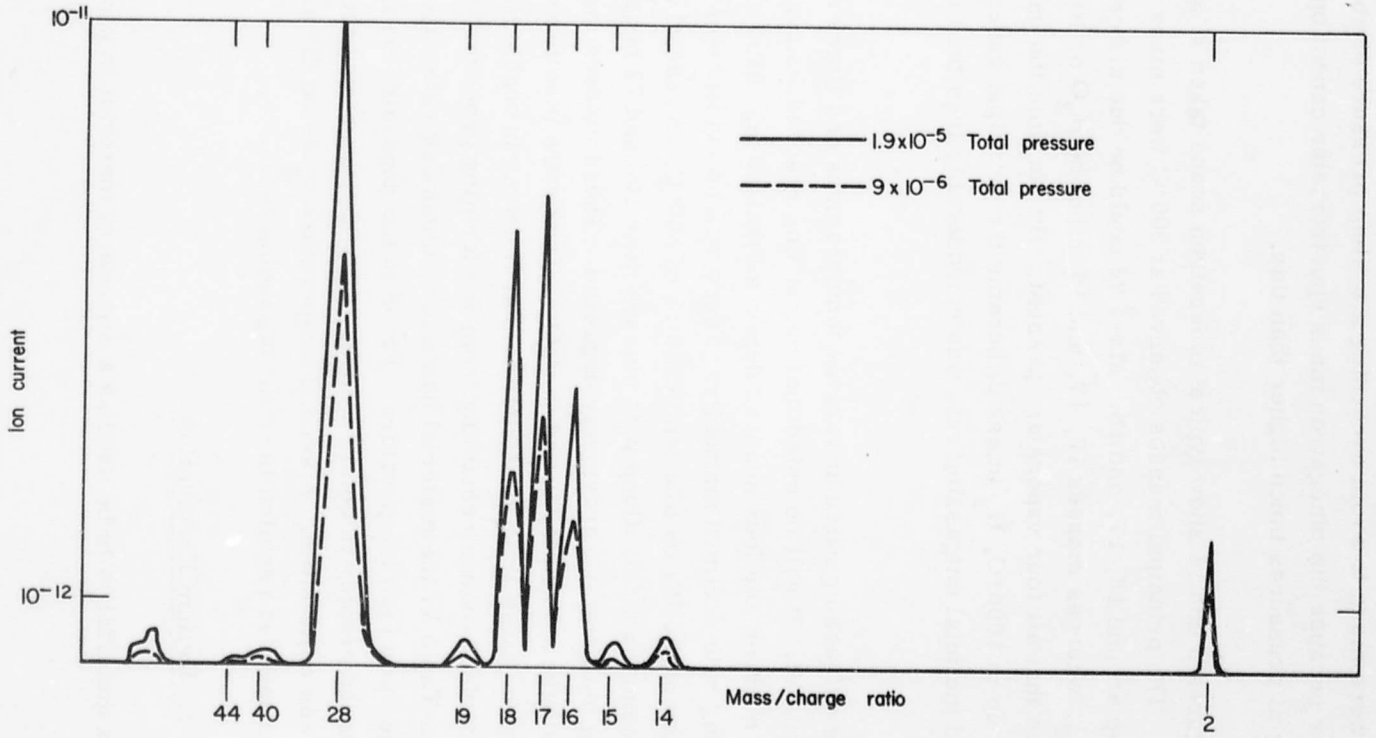
increments were made to avoid exceeding a system pressure of about 2×10^{-5} torr because the omegatron mass spectrometer cannot operate properly at pressures much higher than this.

Figures 11 and 12 show typical omegatron scans taken at 300° and 1000°C. The principal masses observed at 300°C were mass 28, and the group around 18, 17, and 16. Mass 28 could be due either to CO, or to N_2, whereas masses 18, 17, and 16 might be H_2O or NH_3. It is probable that all four vapors are present. By the time the sample was brought up to 1000°C, H_2 (mass 2) became the principal gaseous species, and the total outgassing rate was considerably less than it was at 300°C.

The outgassing rates at various temperatures and times are listed in Table VI. It will be noted that outgassing reached its peak between three hundred and four hundred degrees centigrade. After this the outgassing rate declined markedly. There was no evidence of any decomposition of the BN up to a temperature of 800°C. At 850°C masses centered around mass 36, along with masses near 100 and 72 began to appear using material not previously degassed. These masses may be doubly and singly ionized B_2O_3 and $H_3B_2O_4$. They were mostly removed by degassing for some time at 1100°C so that it seems probable that they came from surface oxides remaining from the forming process. As can be seen from Table VI the material has a low outgassing rate once it has been degassed at a high temperature. Prior to the degassing treatment the BN appeared creamy in color, whereas after the degassing treatment the sample was quite white. A second temperature cycle on the sample after it was degassed resulted in small degassing rates.

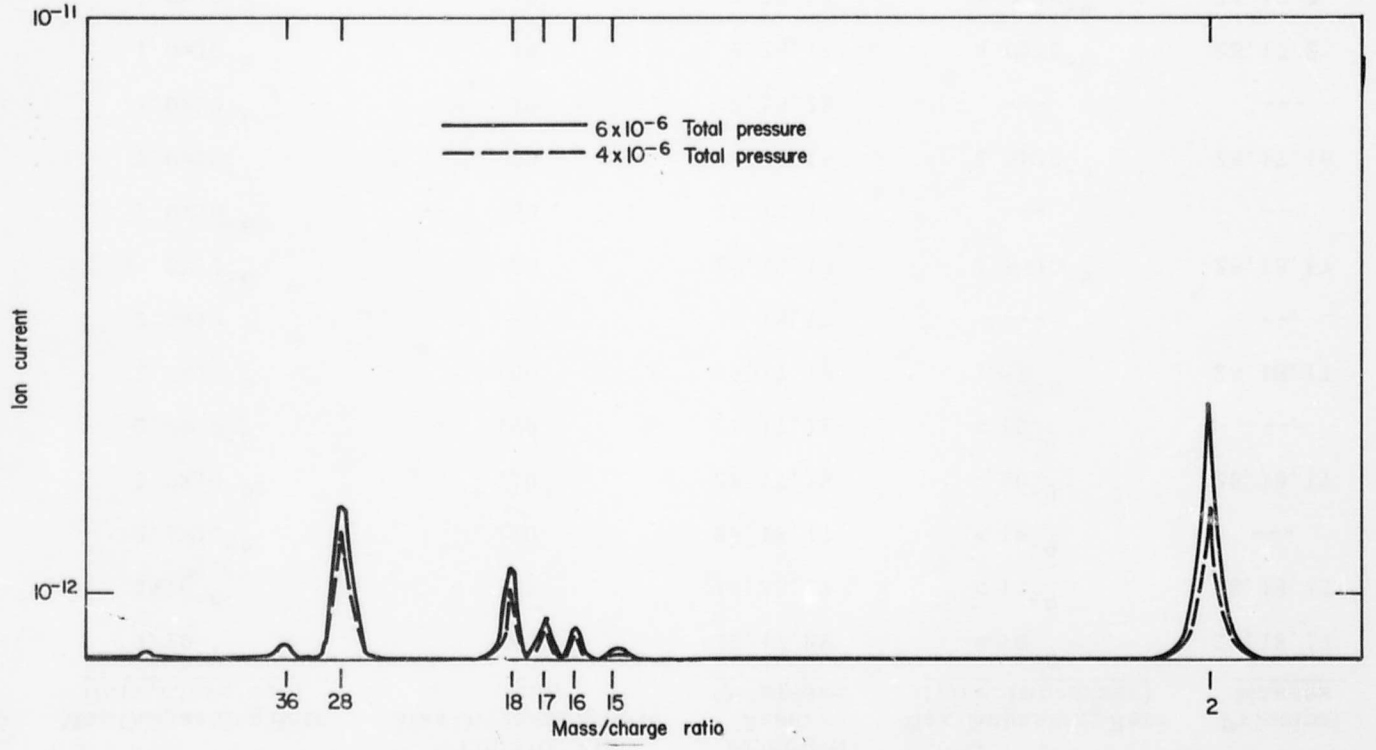
i. Helium Permeation

If a material is to be used as a structural material in a vacuum



Omegatron Scans of BN-27 at 300°C During Initial Degassing

Figure 11



Omegatron Scans of BN-27 at 1000°C During Initial Degassing

Figure 12

TABLE VI

OUTGASSING RATES OF ISOTROPIC BORON NITRIDE (BN-27)

Temp (°C)	Initial Degassing: Max Outgassing Rate (torr, liters/sec)	Initial Degassing: Time to Half Max Outgassing Rate (min)	Initial Degassing: Principal Masses Outgassed	After 1100°C Degassing: Max Outgassing Rate (torr, liters/sec)	After 1100°C Degassing: Principal Masses
100	1×10^{-7}	60	18, 17, 28	$< 10^{-9}$	28, 18, 17
200	2×10^{-6}	120	18, 28, 17	$< 10^{-9}$	28, 18, 17
250	2.5×10^{-6}	140	28, 18, 17	$< 10^{-9}$	---
300	3.0×10^{-6}	130	28, 17, 18	$< 10^{-9}$	28, 18, 17
325	2.0×10^{-6}	190	28, 17, 18	$< 10^{-9}$	---
400	2.5×10^{-6}	100	28, 17, 18	1×10^{-9}	28, 18, 17
450	2.0×10^{-6}	50	28, 18, 17	---	---
500	1.0×10^{-6}	60	28, 18, 17	2.5×10^{-9}	28, 18, 17
600	1.0×10^{-6}	50	28, 18, 17	---	---
700	7.0×10^{-7}	90	2, 28, 18	2.5×10^{-9}	28, 17, 16
800	1.0×10^{-6}	30	2, 18, 28	---	---
900	1.0×10^{-6}	30	2, 28, 18	4.0×10^{-9}	28, 17, 2
1000	1.0×10^{-6}	30	2, 28, 18	6.0×10^{-9}	28, 17, 2

device one of its important properties is obviously its permeability to gases, particularly if it is to be part of the vacuum envelope. A sample of isotropic BN (BN-22) 0.5 mm in thickness showed no detectable helium permeation at room temperature and one atm of helium.

The setup employed is shown in Fig. 13. A sample of isotropic BN (BN-22) previously outgassed at 1500°C was sealed with an epoxy type vacuum cement over a one cm diameter aperture in a stainless steel flange, which in turn was fastened to the vacuum system through a crushed copper gasket. The system was evacuated to a pressure of 10^{-6} torr with 8 liters/sec. ion pump. The omegatron mass spectrometer was adjusted to peak sensitivity for a mass charge ratio of 4, corresponding to helium. Helium at one atmosphere was applied to the outside of the BN for fifteen to thirty minutes but no change was observed in the ion current of the omegatron. The sensitivity of the system is sufficient so that a permeation rate of 10^{-9} torr liters/sec./cm^2 can be detected, consequently the permeation rate was less than that.

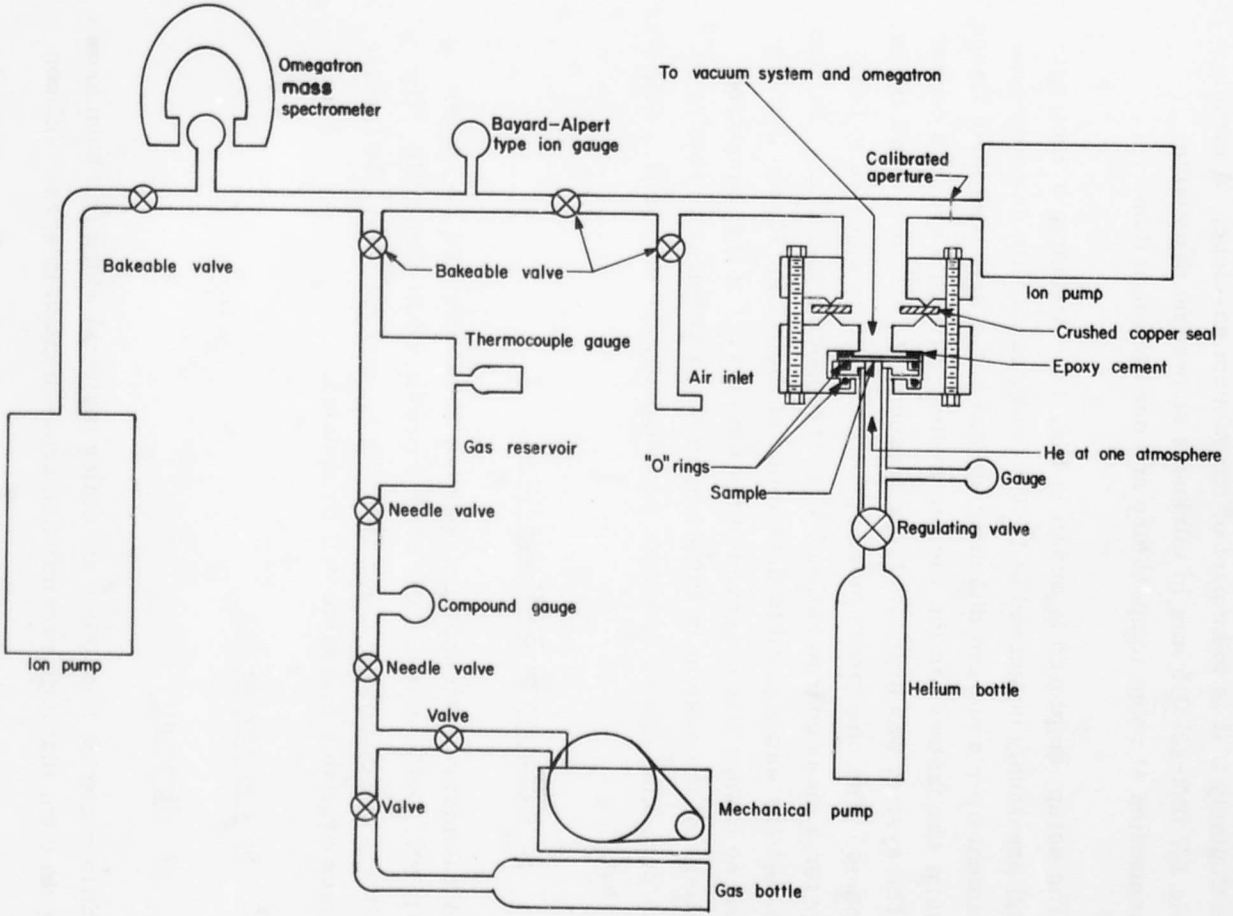
j. Summary of BN Properties

A summary of the known properties of hot-pressed BN, anisotropic CVD BN, and isotropic CVD BN are presented in Table VII. The CVD materials are obviously superior to the hot-pressed BN. As further data becomes available this table will be updated.

C. Silicon Nitride

1. General

Silicon nitride is another insulating material which has been known for a long time but that only recently has aroused much interest. Silicon



Helium Permeation Setup

Figure 13

TABLE VII

PROPERTIES OF BORON NITRIDE

Property	Units	Temp (°C)	Hot Pressed	Anisotropic CVD	Isotropic CVD
Density	g/cc	RT	2.10+	2.2+	1.4
Purity	%		97.0	99+	99+
Porosity	%		7	None	None observable
Oxidation Resist	mg/cm^2	700	10^{-4}	Neg.	---
Loss	1 sec	1000	10^{-3}	10^{-5}	---
		1200		10^{-4}	---
Hydrolysis		RT	Slowly	None	---
Thermal Exp	$°C \times 10^{-6}$	RT-1000	7.5B 0.77A	24c 0.4a	4.0c 4.0a
Thermal Cond	cgs	200	0.08B 0.05A	--- 0.19a	--- 0.2a***
		850	0.07B 0.04A	0.0035c 0.17a	--- 0.2a***
Elec. Resist	Ω cm	RT	10^{13}B	10^{15}c	---
		500	10^{10}B	10^{11}c	---
		1000	10^{4}B	10^{8}c	---
		1500	10^{3}B	10^{5}c	---
Dielec. Const	at 10^{10} cps	RT	4.78*	5.12*	3.36**
		400	4.80*	5.12*	3.38**
		1000	4.87*	5.18*	3.42**
		1100	4.88*	5.19*	3.43**
		1500	---	---	3.47**

*
**Data from Lab. for Insulation Research at MIT.
***Data from Lab. for Insulation Research at MIT at 5.75×10^9 cps.
Tentative Value.

TABLE VII (Cont'd)

Property	Units	Temp (°C)	Hot Pressed	Anisotropic CVD	Isotropic CVD
Loss Tangent	at 10^{10} cps	RT	0.00033*	0.00014*	0.00030**
		400	0.00039*	0.00008*	0.00015**
		1000	0.00297*	0.00005*	0.00005**
		1100	0.01*	0.00005*	0.00007**
		1500	---	---	0.00043**
Flexural Str	psi$\times 10^3$	RT	15	19	14.0 ***
		1000	2	19	12.0 ***
		2000	---	24	---
Compressive Str	psi$\times 10^3$	RT	45	72	---
Elastic Modulus	psi$\times 10^6$	RT	12.3	3.5	1.6-4.8
Poisson's Ratio					0.23-0.27

A Measured parallel to molding pressure
B Measured perpendicular to molding pressure
a Measured parallel to deposition surface
b Measured perpendicular to deposition surface

---

*Data from Lab.for Insulation Research at MIT.

**Data from Lab.for Insulation Research at 5.75$\times 10^9$ cps.

***Deposition Temp 1700°C.

nitride in two phases, alpha and beta, occur together in various proportions in material as usually prepared. The low temperature form (alpha) transforms to the beta phase upon heating at 1400° - 1600°C.

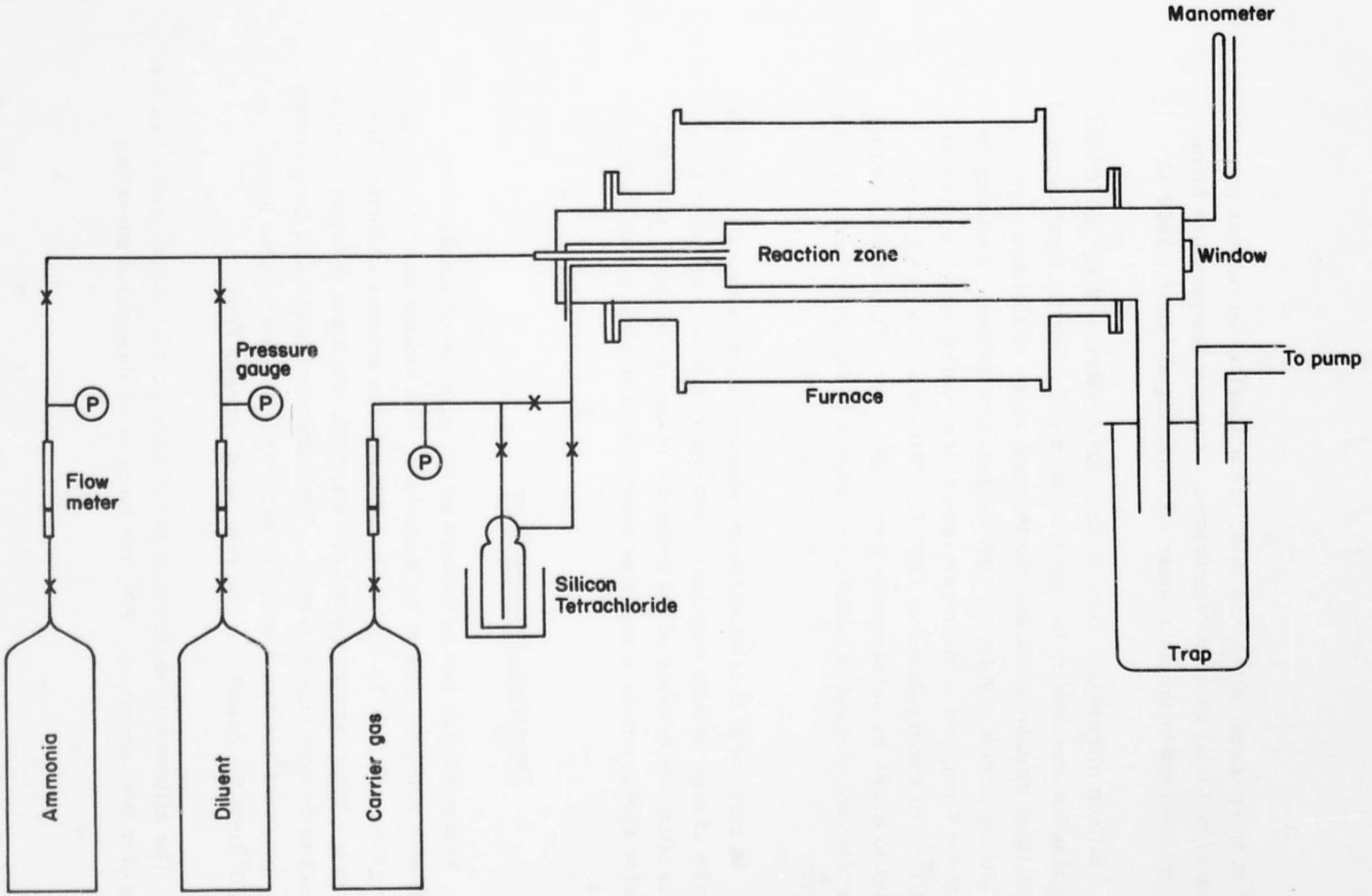
Silicon nitride is a very strong, hard material that, like CVD BN, retains its strength up to high temperatures. The thermal expansion of silicon nitride is low and the thermal shock resistance high. Dense silicon nitride displays a high oxidation resistance, probably because of the formation of an impervious silica coating which serves to protect it up to temperatures of 1400°C. Silicon nitride is also very resistant to attack by substances other than oxygen. It is unattacked by many molten metals and is particularly stable in the presence of molten aluminum.

In pure form it is an excellent electrical insulator, although the resistivity of high density material prepared by ordinary ceramic techniques is often low because of the presence of excess silicon. CVD silicon nitride appears to be a superior electrical insulating material for use in tubes.

2. Deposition Process Runs

Silicon nitride can be formed by the reaction of silicon tetrachloride with ammonia as source materials, with helium and nitrogen as carrier gases. Figure 14 shows the setup used in schematic form. The source gases (plus carrier gases) are directed onto a hot substrate where they react to deposit silicon nitride. The unreacted gases and the gaseous reaction products are removed by a cold trap and a mechanical pump. Table VIII lists the conditions and results of process runs.

The silicon nitride process is not quite as well characterized as the process for the anisotropic BN, but there is no deposition annealing



Silicon Nitride System

Figure 14

TABLE VIII

SUMMARY OF CVD PROCESS RUNS - SILICON NITRIDE

Deposition Conditions

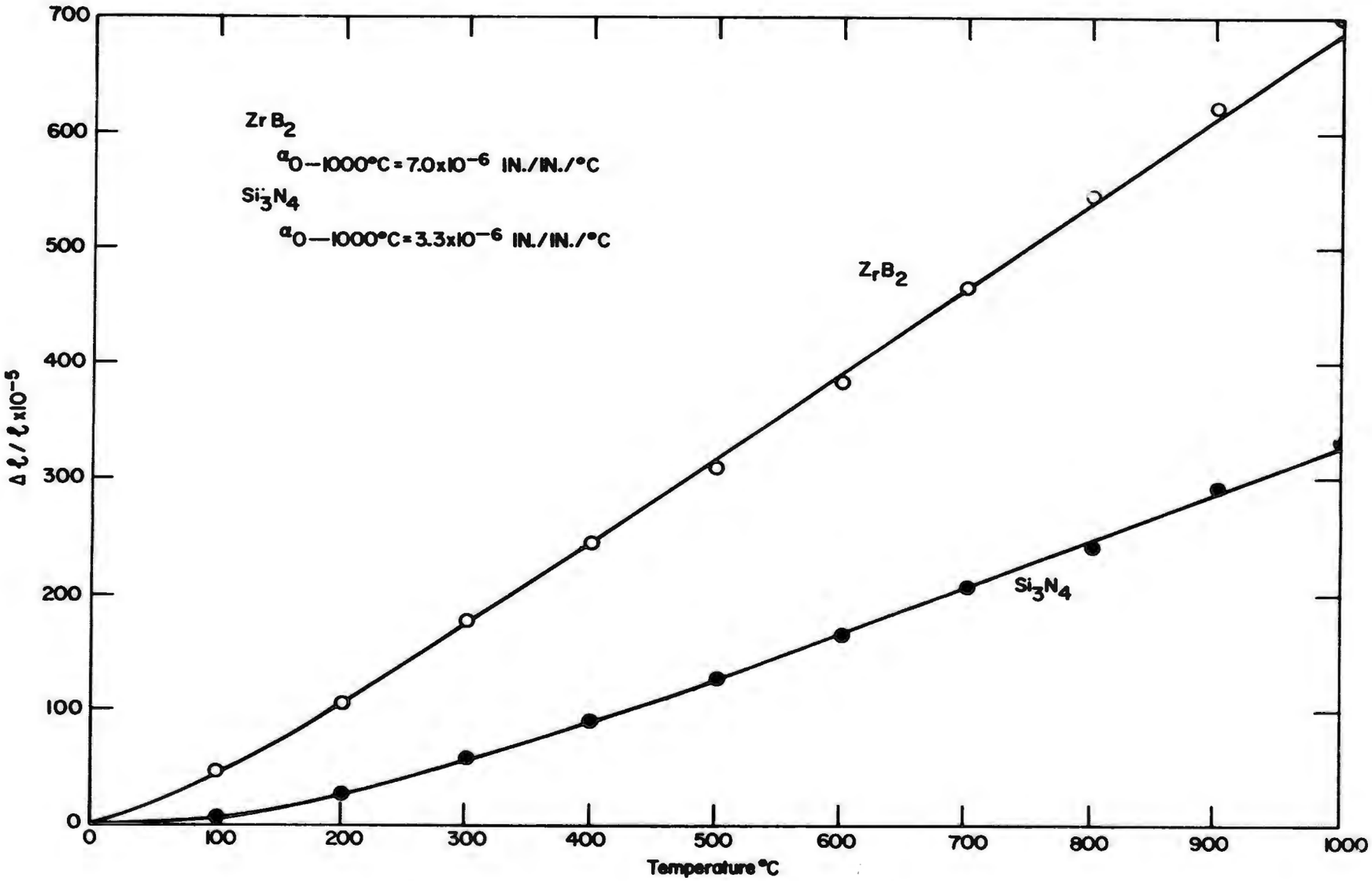
Average Flow Rates (liters/min)

Run Number	Temp (°C)	Time (hrs)	Silicon Compound	Carrier He	NH_3	Carrier He	Pressure Average (torr)	Rates Max (mils/hr)	Remarks
SN-13	1270	21	0.12	0.30	0.1	0.5	12	2.2	
SN-14	1260	19	0.10	0.30	0.4	0.5	11	1.0	two layers one clear-one milky
SN-15	1260	14	0.06	0.20	0.7	0.2	11	2.0	Clogged trap
SN-16	1270	12	0.06	0.20	0.7	0.3	5	2.0	Clogged trap
SN-17	1270	12	0.05	0.15	1.4	0.15	5	1.1	Clogged trap

problem. The material is crystalline with little preferred orientation. The deposit is sometimes granular and white in appearance. When homogeneous, the deposit is glassy in appearance, has a density of 3.18, and is dark due to the use of a graphite substrate. Above about 1300°C the deposit reacts slowly with graphite to form silicon carbide.

Difficulties were experienced in obtaining samples with sufficient thickness for meaningful property measurements because of run termination resulting from clogging of the trap. Analysis showed the clogging material to be ammonium chloride. The series of runs shown in Table VIII proved that decreasing the relative ammonia-silicon tetrachloride ratio resulted in less clogging and longer runs, without deleteriously affecting the product. Thus it is concluded that the clogging problem can be eliminated by reducing the ammonia flow.

Figure 15 shows the thermal expansion of a sample of CVD Si_3N_4.



Thermal Expansion of CVD Si_3N_4 and ZrB_2

Figure 15

IV. CVD CONDUCTING MATERIALS

A. CVD Borides

Electrodes in vacuum tubes are generally exposed to intense electron bombardment, and therefore should be refractory, chemically resistant, have good vacuum properties, and should be resistant to the formation of surface insulating films. Obviously, they should also have good electrical and thermal conductivities, and have a low primary and secondary emission. CVD borides may be useful for electrode applications, either alone or as a coating upon some other refractory material.

Probably the most important characteristic possessed by some of these substances is their extremely low secondary emission. We have measured the secondary emission ratio of CVD TiB_2 and found it to be approximately 0.6 at its voltage maximum. Since TiB_2 is extremely refractory, possesses metallic conduction, and has good vacuum properties it should be an excellent electrode material for heavy duty applications.

CVD TiB_2 and ZrB_2 are deposited by introducing titanium (or zirconium) tetrachloride, boron trichloride, and hydrogen into the furnace in the appropriate molar ratio. Table IX shows the process conditions for some of the zirconium boride runs which we have made.

Figure 16 is a metallograph at magnification of 100 of ZrB_2 deposited at 1850°C. (Boride run no. 1). The layered structure, seen in this photograph, resulted from variations in the input flow rate of $ZrCl_4$ vapor, a problem we have recently corrected.

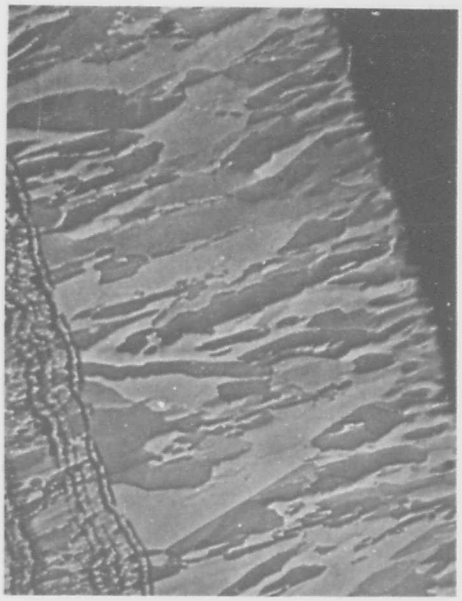
The secondary emission ratio and some of the other pertinent properties of the CVD borides are being measured and will be reported as they become available.

TABLE IX

PROCESS RUNS - CVD BORIDES

Zirconium Diboride

Run No.	Density (g/cm^3)	Deposition Temp (°C)	Pressure (mm)	BCl_3 (lpm)	H_2 (lpm)	$ZrCl_4$ Feed Rate (g/min)
1	6.00	1850	7	0.25	2.5	1.35
2	5.82	1700	3	0.25	2.5	1.55
3	5.78	1700	8	0.25	7	1.67
4	5.00	1700	8	0.25	7	1.36
5	5.69	1800	6	0.25	7	1.00



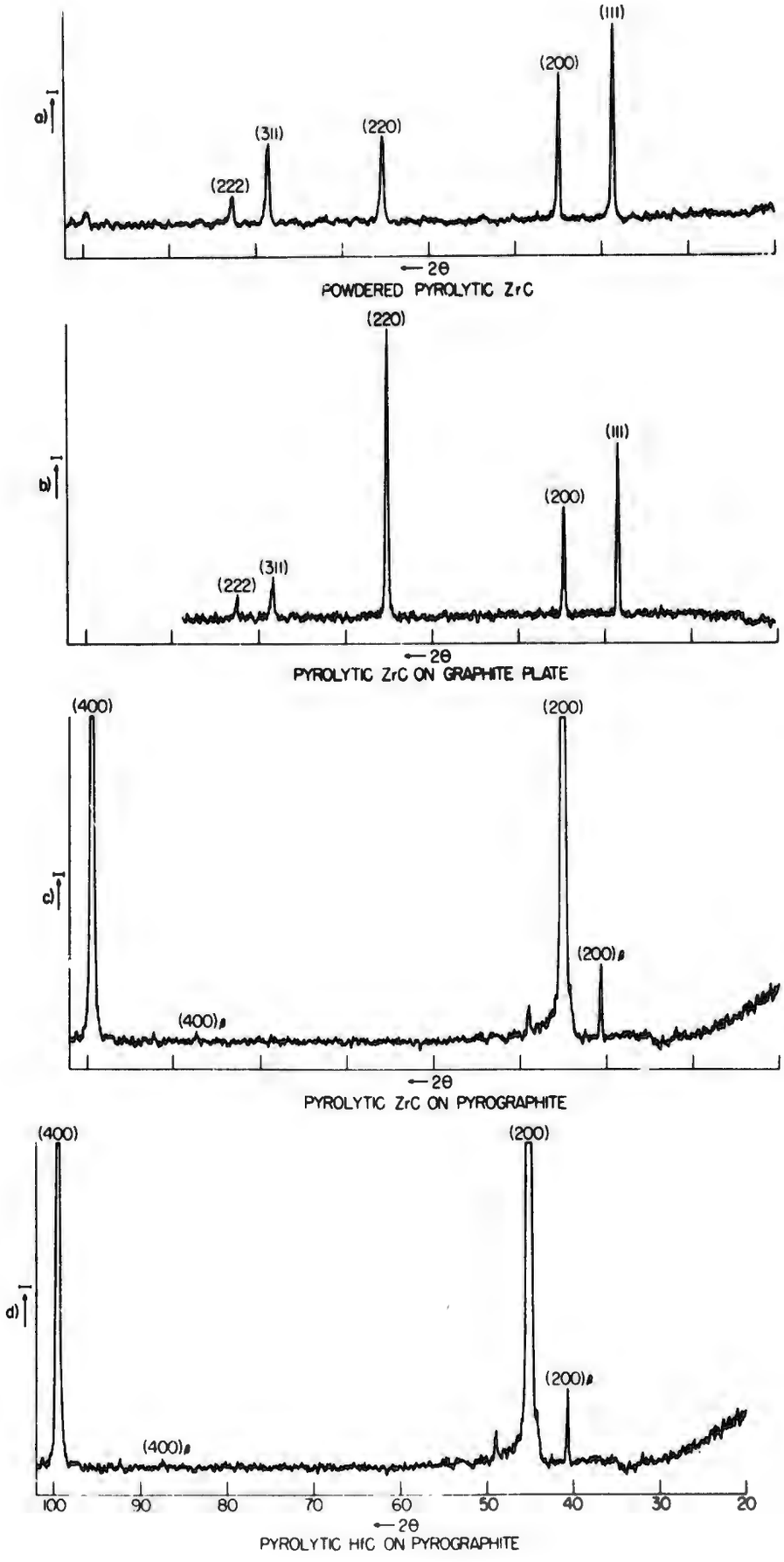
Metallograph of CVD ZrB_2 at a Magnification of 100X

Figure 16

B. CVD Carbides

Metal carbides can be vapor deposited by the reaction of the appropriate metal halide with a hydrocarbon. Lepie[13] has studied the preparation of CVD ZrC from the reaction of zirconium tetrachloride vapor with methane on the surface of a hot graphite substrate. Zirconium carbide has a cubic structure; however, it can be vapor deposited with certain planes having high degrees of preferred orientation. Figure 17 shows x-ray diffraction patterns for CVD ZrC and HfC samples in which strong orientations in the ⟨100⟩ and ⟨110⟩ directions are observed. The properties of some potentially useful carbides are shown in Table X. Some of the carbides may be useful as long life cathodes for electron tubes.

We have cut discs ultrasonically from two of the ⟨110⟩ samples of ZrC, mounted them in tantalum sleeves, and inserted them as cathodes in a diode assembly. The ZrC cathode was indirectly heated with a tungsten heater, and a guard ring and anode was fabricated from molybdenum. The entire assembly was inserted in a clean vacuum system, which after a 300°C bakeout, attained a pressure of 5×10^{-9} torr. Thermionic emission measurements were made as a function of cathode temperature and anode voltage, and a Richardson plot was made of the results. The data indicates a work function of about 2.2 eV, although the A value is low. Work functions for zirconium carbide in the conventional randomly oriented polycrystalline form are reported to be between 2.2 and 4.2 eV.[14] One would expect certain crystallographic faces of these materials to have higher or lower work functions. Measurements of the thermionic emission properties of CVD carbides are continuing.



X-Ray Diffraction Patterns of Pyrocarbides Illustrating Variations in Preferred Orientation

Figure 17

TABLE X

PROPERTIES OF CARBIDES

Property	Units	Temp (°C)	ZrC	CVD ZrC	HfC	CVD HfC	TiC
Melting Temp	°C		3375		3890		3250
Density	g/cc	RT	6.8	6.3	12.2	12.7	4.9
Therm Exp	$°C \times 10^{-6}$	RT - 1000	6.7	6.3	6.0	6.9	7.7
Therm Cond	kgs	RT - 100	0.058	0.107	0.049	---	0.053
Elec Resist	μcm	RT	63	37	109	52	104
Hardness	kg/mm^2	RT	1830	2356	1940	1960	2620
Flex Strength	$psi \times 10^3$	RT	24	12	34	48	87
Comp Strength	$psi \times 10^3$	RT	238	---	---	---	196
Elastic Mod	$psi \times 10^3$	RT	45	---	61	---	60
Work Function	eV		2.2 - 4.2	2.2	4		4.1

V. CONCLUSIONS

Isotropic CVD BN may be a very important new material for electronic applications. Our results indicate that it has a relatively high thermal conductivity (about the equivalent of nickel) even at 1000°C, and has good dielectric properties to at least 1500°C. It displays an excellent thermal shock resistance because of its low modulus of elasticity, and relatively low coefficient of thermal expansion. Its coefficient of thermal expansion is isotropic and is approximately equivalent to that of tungsten between room temperature and 1000°C, thus is should be relatively easy to make a metal-insulator seal by conventional techniques. It displays good vacuum properties and is impermeable to helium. Isotropic CVD BN is readily fabricated into nearly any specific shape required, and it is easily machinable using conventional metal-working tools.

Mass spectrometer studies show no evidence of decomposition of isotropic CVD BN up to a temperature of 850°C. At 850°C masses which may be due to doubly and singly ionized B_2O_3 and $H_3B_2O_4$ begin to appear from material not previously outgassed. These masses can mostly be removed by degassing at 1100°C, so it seems probable that they came from surface oxides remaining from the forming process. After an initial degassing at 1100°C CVD BN shows a low outgassing rate even at elevated temperatures.

Electron microscopic examination showed that isotropic BN appears to be made up of randomly oriented platelets with a fairly uniform size of about one-quarter micron. This is consistent with the fact that the measured properties were almost isotropic, and also with x-ray results which showed virtually no preferred orientation. Although the density of isotropic CVD BN is only about 0.6 of that theoretically expected, specimens showed no identifiable porosity under metallographic examination at the highest possible magnification. Since no helium permeation of a thin sample could be detected at a differential pressure of one atmosphere,

any pores which do exist must be non-interconnecting. No evidence was found by x-ray diffraction for the presence of rhomobohedral BN in isotropic CVD BN. The high temperature strength and the density of isotropic CVD BN deposits appear to depend upon the deposition temperature.

Optimum materials ratios have been determined for the formation of anisotropic CVD BN at deposition temperatures ranging between 1500° and 1900°C. "Bowing" during the deposition of anisotropic BN was solved by laying down a flash coat of isotropic BN on the substrate prior to starting the deposition from BCL_3. Plates of CVD BN one-quarter inch in thickness have been formed of both isotropic and anisotropic material. Our results indicate that anisotropic CVD BN can be formed (after some experimentation) into any specific shape whose thickness is not greater than ten percent of its radius of curvature, by following the same general principles which have been developed for pyrolytic graphite.

CVD zirconium carbide ⟨110⟩ orientation has a work function of 2.2 eV as compared to work functions reported for conventionally prepared ZrC between 2.2 and 4.2 eV.

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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Raytheon Company
Waltham, Massachusetts

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

N/A

3. REPORT TITLE

CHEMICAL VAPOR DEPOSITED MATERIALS FOR ELECTRON TUBES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

First Quarterly Report - 15 May - 14 Aug 65

5. AUTHOR(S) (Last name, first name, initial)

Steele, S. R.; Pappis, J.; Ellis, R.; Hagen, L.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
October 1965	56	14

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA 28-043 AMC-01343 (E)	S-803
b. PROJECT NO. 1P6-22001-A-055-01	
c. Task-01	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. Subtask-11	ECOM-01343-1

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
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13. ABSTRACT

This program was established to investigate chemical vapor deposition as a method of producing materials or coatings for use in vacuum electron devices.

Experiments have been conducted with two methods of producing CVD BN, one resulting in a product with isotropic properties, the other anisotropic properties. Depositions have been made at temperatures ranging from 1350° up to 1900°C. BN deposits 1/4 in. and more have been obtained on the interior of a 2X2X10 in. graphite box. Experiments were made with various surface finishes of the substrate. Our results indicate that, by following the same general principles which have been developed for pyrolytic graphite, anisotropic BN can be formed after some experimentation into any specific shape whose thickness is not greater than 10% of its radius of curvature.

Several properties of isotropic CVD BN have been measured. Preliminary measurements of its thermal conductivity show it to be about equivalent to nickel, and its thermal expansion nearly matches that of tungsten. The modulus of elasticity is low, consistent with a high thermal shock resistance. Flexural strengths average about 10,000 psi. X-ray examination showed no preferred orientation. No helium permeation was obtained, and degassing studies demonstrated good vacuum properties at least to 1000°C.

Some experiments have been conducted with CVD silicon nitride and zirconium diboride. CVD TiB_2 has a secondary emission ratio of 0.6.

A work function of 2.2 eV has been measured for CVD ZrC with a $\langle 110 \rangle$ orientation.

DD FORM 1 JAN 64 1473

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14 KEY WORDS	LINK A		LINK B		LINK C	
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