LA-UR -82-3276

LA-UR--82-3276

DE83 003567

Conf-821147--1

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SUBMITTED TO

The First International Conference on Plasma Chemistry and Technology
November 17, 1982
San Diego, CA

DISTRIBUTION OF [illegible]

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THIN FILMS FROM AMMONIA-BORANE

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ABSTRACT

A low pressure N_2 plasma treatment of ammonia borane (H_3NBH_3) or its pyrolysis products [$(H_2NBH_2)_n$, $(HNBH)_n$] generates boron nitride compositions of empirical formula BNH. The process is conducted at essentially room temperature and involves the use of a stable commercially available starting material ammonia borane.

INTRODUCTION

Generation of thin polymeric films and coatings containing a high content of boron and nitrogen may be accomplished in several different ways. According to an early report subjecting borazine vapor to a radiofrequency discharge formed monomeric H_2BNH_2 (among numerous other products) which polymerized spontaneously between -196 and -155°C.[1] The product, an "inert white solid," was believed to be $(H_2NBH_2)_n$ although only its infrared spectrum was reported. A subsequent report from the same laboratory described the formation of, presumably, the same product by the vapor phase pyrolysis of an entirely different starting material, ammonia-borane (H_3NBH_3), but no experimental details of the preparation were given.[2]

We have developed an improved synthesis of poly(ammonia-borane) by the vapor phase pyrolysis of H_3NBH_3 and have conducted a detailed characterization of the material.[3-5] We have also generated a high nitrogen (56 wt.%) content polymeric material by subjecting H_3NBH_3 or its pyrolysis product[5,6] to a low pressure N_2 plasma. Here, we wish to report on the low pressure plasma (LPP) approach to high boron and nitrogen content films and coatings.

EXPERIMENTAL

Materials

Commercial H_3NBH_3 (Callery Chemical Co.) was vacuum and zone-sublimed until the melting point was raised to 115-116°C.

Nitrogen was Matheson high purity (99.99%) grade, used as received.

Film Deposition

H_3NBH_3 Films. H_3NBH_3 may be sublimed (at ~ 45°C) onto a glass substrate as a uniform film only if done in a dynamic vacuum of at least 10^{-5} torr. In the solid state, H_3NBH_3 is stable to at least 70°C and TGA indicates significant decomposition starting at just above 110°C.[7] Typical film thicknesses varied between 10-50 μm.

$(H_2NBH_2)_n$ Films. In the preparation of the polymeric H_2NBH_2 films, measured amounts (0.02 to 0.10 g) of H_3NBH_3 were placed in the bottom section of a commerical glass vacuum sublimer which had been modified by the addition of a 1 inch (dia.) x 6 inch test tube end to the bottom of the apparatus directly below the cold finger. The apparatus was evacuated to 1 x 10^{-3} torr or less and back filled with dry nitrogen to a pressure of 2-3 torr. The nitrogen was necessary to prevent rapid sublimation of H_3NBH_3 and to facilitate its thermal decomposition.

The substrates (for example, microscope cover glass) to be coated were attached to the cold finger. For infrared analysis NaCl plate was attached to the cold finger. To begin the decomposition, the sublimer was closed and the tip containing H_3NBH_3 immersed in a stirred oil bath at 130-140°C. Liquid nitrogen was placed in the cold-finger of the sublimer as heating was begun. Within 60-90 seconds, a rapid frothing decomposition of the fused H_3NBH_3 commensed releasing noncondensible gas, presumably H_2, and depositing a white coating on the microscope cover glass as well as the cold finger.

The [illegible]e solid product was allowed to form for up to five minutes during which time hydrogen was pumped away periodically, then the heating bath was removed and the closed sublimer allowed to equilibrate thermally. The white solid was not apparently air sensitive or hydroscopic.

The hydrolyzable hydrogen content of the product was determined by hydrolysis with aqueous HCl at 120^0 for two weeks followed by measurement of the hydrogen in a calibrated Toepler system. The boron content was determined by Parr peroxide fusion followed by titration of the mannitol complex. Calcd. for BNH_4: B, 37.6; H (hydridic) 7.00. Found: B, 37.9; H, 6.97.

$(HNBH)_n$ Films. For the deposition of $(HNBH)_n$ films the following modifications to the above described procedure were introduced. The system was evacuated to ~ 10^{-3} torr, but was not backfilled with dry N_2. The film deposition was done in dynamic vacuum. The test tube end to the vacuum sublimer was wrapped with two separate heating tapes. The heating tape closer to the cold finger was kept at ~ 350^0C and the bottom heating tape was kept at ~ 120^0C. This heating arrangement resulted in a more extensive pyrolysis and, hence, the formation of NBH_2. The nitrogen content in these materials was determined directly by a neutron activation technique or the deposited materials.

Low Pressure Plasma Treatment

The LPP instrument that we are using has been described before.[8-10] Typical operating parameters that we were using in converting the white, opaque ammonia-borane films into transparent, glass-like films were:

Initial pressure	10 m torr
Operating system pressure	400 m torr
N_2 flow rate	100 sccm
Current	4 mA
Voltage	305 V

Typical treatment times (dependent upon the sample size) varied from 2 16 hours. The three types [H_3NBH_3, $(H_2NBH_2)_n$, $(HNBH)_n$] of films were transferred in open air to the plasma chamber and were typically positioned in the center of the bottom electrode.

We are also using optical emission spectroscopy (Plasma-Therm, Inc., Plasma Scan System, Model PSS-2M) to monitor the plasma composition during the treatment process.

RESULTS AND DISCUSSION

Thermal pyrolysis of H_3NBH_3 when conducted at two different temperatures (140° and 350°C) and different vacuum conditions yielded essentially pure $(H_2NBH_2)_n$[5] or $(HNBH)_n$.[6] Further variation in pyrolysis temperature or vacuum conditions, however, did not result in the generation of pure boron nitride. Pyrolytic boron nitride has been generated by a variety of techniques; however, even the more recent techniques involve synthetic difficulties. For example, if borazole, $B_3N_3H_6$, is heated to 500°C, it undergoes pyrolysis and eliminates hydrogen to give a non volatile material of expirical formula BNH. If this material is further held at 900°C, it loses hydrogen to yield a product of composition approaching that of BN.[11,12]

The use of low pressure plasma to generate boron nitride does not seem to have been reported. We have found now that low pressure nitrogen plasma treatment of 12 to 24 μm thick H_3NBH_3 films converts them into (H_2BNH_2) and other compositions approaching BN depending upon the length of the treatment time. For example, a N_2 plasma (400 m torr, 80 sccm, 4 mA, 3 hours) treatment of a 24 μm thick H_3NBH_3 film gave a hazy or translucent film that had an IR spectrum essentially identical to that of a material obtained by pyrolysis[5] (Table I). The translucent film did have several other bands that the opaque (H_2NBH_2) film did not possess and had strong characteristic absorptions typical of BN (1390, 810, 720 cm^{-1}). The assignment of all the peaks is undergoing further study. Furthermore, the spectra compared rather well with those reported for a polymeric amminoborane prepared by a completely different route.[1] If the LPP treatment at the above conditions is continued for longer time (up to 16 hours) or an rf generated plasma at power levels of up to 150 watts is used, a completely transparent, uniform film is generated. Material that has been plasma treated for longer times or at higher power densities analyzed for the empirical formula of $BNH_{0.5}$. The nitrogen concentration in the materials was determined directly on approximately 1 g samples by a neutron activation technique. These are the mildest conditions (at essentially room temperature) that are found to generate a material that is essentially BN. Furthermore, the starting material is commerically available, inexpensive, stable, and is easy to handle.

Literature reports the generation of transparent BN films by pyrolysis of BCl_3 + NH_3 mixtures at 800-1500°C[13,14] and of 2,4,6-trichloroborazine.[15,16] In one approach molybdenium and tungsten substrates were heated to 770-1300°C to pyrolyze the trichloroborazine vapors.[16] At temperatures above 800°C vitreous, transparent BN films were deposited. In the BCl_3 + NH_3 approach products from gray-black to yellow-brown to white-feathery to translucent to clear-glassy films were all possible depending upon the reactant ratio, their transport rate, pyrolysis temperature (1300° to 1700°C), and deposition chamber geometry used. The two types of products that we have generated: translucent and clear-glassy, fit into this range of observed products (Figs. 1 and 2).

The density of the reported BN has been found to vary from 1.846 to 2.262 g/cm depending upon the preparation conditions. The lower density materials are presumed to have nucleated in the gas phase with the microcrystallite growth occuring in the gas phase before their deposition. We find that compacting (24,000 psi at 100°C) material into a pellet gave a "pellet" density of 1.23 g/cc. As our technique, presumably, does not involved gas phase nucleation the low density is only a reflection of the quality of the pellet. While the H_3NBH_3 and $(H_2NBH_2)_n$ materials decompose violently in concentrated HCl solution, the material with empirical composition of $BNH_{0.5}$ was insoluble and stable indefinitely in concentrated HCl solution.

We are using optical emission spectroscopy to monitor the plasma composition above the substrate during the treatment process to elucidate possible reactions mechanisms during the treatment. These studies are continuing and will be the subject of a future report.

CONCLUSION

A new low temperature (essentially room temperature) synthesis procedure for an essentially boron nitride composition has been developed. The technique involves the use of low pressure N_2 plasma in the treatment of thin films of ammonia borane (H_3BNH_3) or its pyrolyses products [$(H_2NBH_2)_n$, $(HNBH)_n$] and the generation of compositions with empirical formula of $BNH_{0.5}$.

ACKNOWLEGEMENT

The authors express their appreciation to Bob Day for his interest and valuable discussions on this project.

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TABLE I

INFRARED SPECTRAL BANDS OF POLY(AMINOBORANES)

Thermal Pyrolysis cm^{-1}	Low Pressure Plasma cm^{-1}	$(H_2NBH_2)_n^a$ cm^{-1}
3240-3300	3250-3300	3280
2280-2400	2300-2400	2380
1560	1560,1620 sh	1560
1375-1400	1340-1400	1390
1160-1200	1175-1210	1180
1050-1080	1050-1080	1060-1090
---	975	970
---	940	---
840	840	840
---	700	---

a. From Ref. 1.

FIGURE CAPTIONS

1. H_3NBH_3 Film on Glass Slide
2. Translucent Film After LPP Treatment of H_3NBH_3 Film

Figure 1

Figure 2