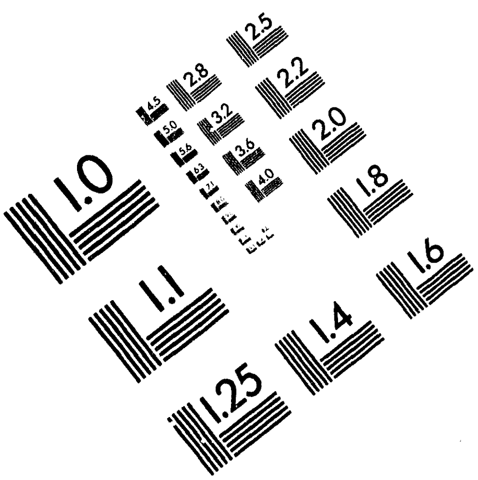
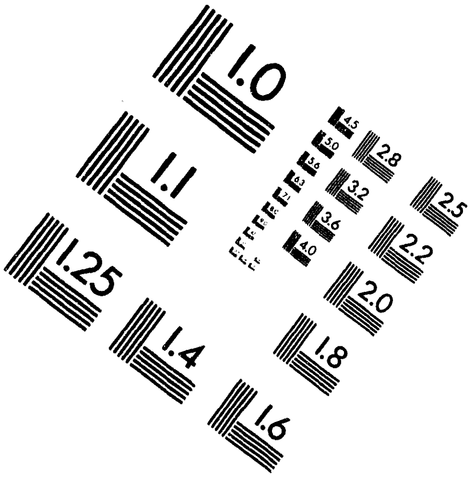


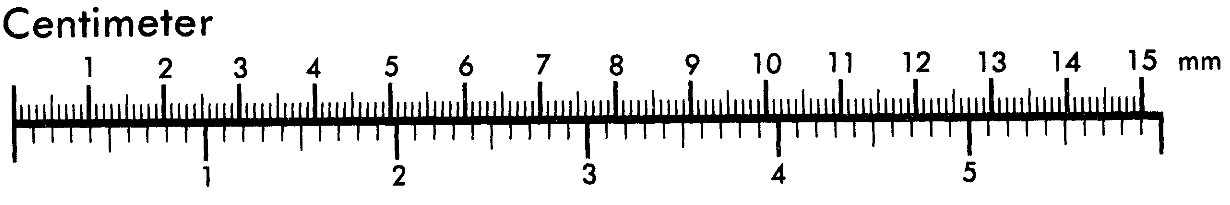
AIIM

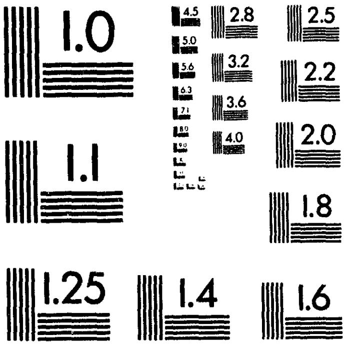
Association for Information and Image Management

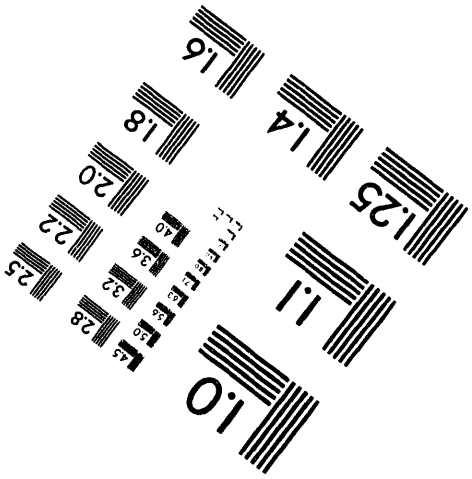
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

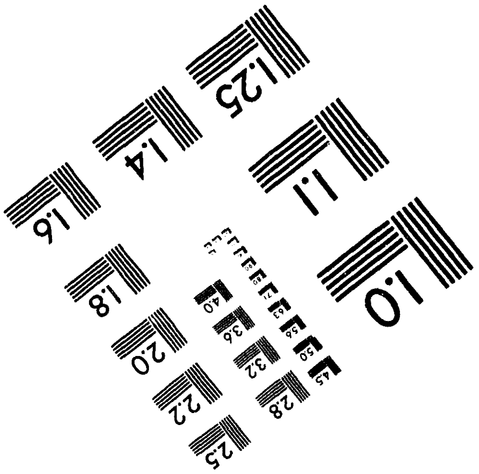
301/587-8202











MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

SAND--94-8620C
Conf-940440--4

Effects Of Ambient Conditions On The Adhesion Of Cubic Boron Nitride Films On Silicon Substrates

G.F. Cardinale[†], P.B. Mirkarimi[‡], K.F. McCarty[‡], E.J. Klaus[‡], D.L. Medlin[‡], and D.G. Howitt[†]
[†]University of California, Davis, CA 95616, [‡]Sandia National Laboratories, Livermore, CA. 95550.

We have investigated the influence of environmental conditions on cubic boron nitride (cBN) film adhesion to silicon substrates. cBN films were deposited onto (100)-oriented silicon substrates by ion-assisted pulsed laser deposition. The irradiating ions were mixtures of nitrogen with (i) argon, (ii) krypton, and (iii) xenon. Under room-ambient conditions, the films delaminated in the following time order: N/Xe, N/Kr, and N/Ar. cBN films deposited using N/Xe ion-assisted deposition were exposed to four environmental conditions for several weeks: a 1-mTorr vacuum, high humidity, dry oxygen, and dry nitrogen. Films exposed to the humid environment delaminated whereas those stored under vacuum or in dry gases did not. Films stored in dry nitrogen were removed after nearly two weeks and placed in the high-humidity chamber; these films subsequently delaminated within 14 hours.

I. INTRODUCTION

Cubic boron nitride (cBN) has gained considerable attention in recent years because of its excellent properties including high elastic modulus, high thermal conductivity, and high electrical resistivity. Applications for cBN include cutting tool coatings, integrated circuit fabrication, both as a substrate heat sink and the active device region, and x-ray lithography mask materials[1]. The structure and properties of cBN are similar to diamond, however, cBN has several unique properties including high oxidation-resistance, the ability to be doped with p- and n- type dopants, and a low reactivity with ferrous metals. However, until recently, a major disadvantage has been the difficulty in synthesizing thin films of cubic boron nitride.

Thin film applications of BN are also limited by adhesion. In fact, cubic boron nitride films deposited under certain conditions have been reported to have poor adhesion to various substrates such as tungsten carbide, titanium nitride, stainless steels, and fused silica[2,3,4,5], and on silicon substrates in particular[6]. The delamination was primarily attributed to large compressive stresses in the BN films, however, these reports did not discuss environmental effects on the delamination characteristics. Other reports[7,8] indicated that the formation of boron buffer layers at the silicon-BN interface, namely Si/B/BN_x/cBN structures, improves the adhesion of the BN films significantly. In the present investigation, the influence of environmental effects and film stress (related to deposition conditions) on the delamination of BN films from silicon substrates is discussed. A model for the mechanism of BN delamination is presented, and a comparison with experimental results is discussed.

II. EXPERIMENTAL:

Boron nitride films were deposited onto (100)-oriented silicon substrates by an ion-assisted pulsed laser deposition (IAPLD) technique. A detailed description of this IAPLD system is given elsewhere[9,10]. Pyrolytic hexagonal boron nitride (hBN) targets were ablated with a KrF laser (248-nm wavelength) with 30-nS pulses of approximately 25 to 30 mJ per pulse. Using a 3-cm-diameter Kaufmann-type ion source, the growing film was irradiated with three mixtures of ions: nitrogen and argon ("N/Ar" films), nitrogen and krypton ("N/Kr" films), and nitrogen and xenon ("N/Xe" films); the ratio of nitrogen to inert gas was maintained at 60% nitrogen to 40% inert gas in all cases. The purity of the gases was greater than 99.999%. In all experiments, the cleaned silicon substrates were heated to 400 °C, and the temperature was monitored using a thermocouple mounted to the back side of the substrate. The energy of the ion irradiation was 1 keV.

Using Fourier Transform Infrared (FTIR) spectroscopy, the fraction of cBN in each film was estimated. IR spectra were obtained in reflection with the illumination at near-normal incidence. These spectra were ratioed to a spectrum of a silicon substrate that was cleaned in the same manner as for film depositions. The differently bonded BN phases have characteristic IR features: sp^2-bonded BN (as in the crystalline graphite-like phase hBN or poorly crystalline, turbostratic BN) which has a TO mode absorption at 1370 cm^{-1} attributed to out-of-plane[B-N-B] bending and a TO mode absorption at 800 cm^{-1} due to in-plane [B-N] stretching[11], and sp^3-bonded BN (i.e. cBN) which has a restrahlen TO mode at 1065 cm^{-1}.[12] By taking the ratio of the cBN peak height to the sum of the cBN peak plus the hBN peak height at 1370 cm^{-1}, the relative amount of cBN can be calculated. This procedure is supported by computer simulations which have indicated that the IR sensitivity factors are approximately equal for hBN and cBN films on silicon[10].

Once the amount of cBN in the samples was determined, each sample was scribed and separated into pieces, which were subsequently placed in one of four environmental chambers: vacuum (~ 1 mTorr), dry oxygen, dry nitrogen, and saturated water-vapor formed by bubbling helium gas through distilled water. The dry-gas and water vapor chambers consisted of a glass beaker inside a sealed glass cylinder with a gas inlet and exhaust port. The vacuum vessel consisted of a glass desiccator pumped with a mechanical roughing pump that achieved and maintained approximately 1 mTorr pressure for the duration of the experiment. Figure 1 illustrates the environmental vessels and sample locations.

Film stress was calculated using a "bending-beam" analysis through a modified version of the Stoney[13] equation:

$$\sigma_f = \frac{4\,E_s}{3\,(1 - \nu_s^2)}\,\frac{t_s^2}{t_f}\,\frac{\delta}{L^2}\ ,$$

where σ_f is the film stress, E_s and ν_s are the Young's modulus and Poisson ratio of the substrate, respectively, t_s and t_f are the substrate and film thickness, resp., δ is the maximum deflection of the rectangular beam, and L is the beam length. This equation assumes that $L \gg \delta$, which holds for the measured deflections (~1 µm) and substrate lengths (1 cm). We use a modified Stoney equation (which includes the plate modulus, $E/(1-\nu^2)$ rather than the biaxial modulus $E/(1-\nu)$) since it has been suggested[14] that under the conditions of a rectangular substrate, a relaxed film would take the shape of a cylindrical shell rather than a spherical cap. Substrate deflection was measured using a stylus profilometer, and the film thickness was measured at three wavelengths with an ellipsometer. Substrate dimensions were measured at several locations using a calibrated micrometer and averaged. Using the proper elastic constants for (100) silicon[15], the film stresses were calculated and found to be in the range of 1 to 10 GPa (compressive).

Film delamination was detected by visual inspection at predetermined intervals. Optical and scanning electron micrographs were then taken to record the details of the delaminated BN films.

III. RESULTS:

By exposing the films to room atmospheric conditions, i.e., not stored under vacuum or dry-gas conditions, the delamination occurred roughly within the following times: N/Xe-less than a week, N/Kr-less than two weeks and N/Ar-more than two weeks. Since the N/Xe films tend to delaminate in the shortest amount of time under these ambient conditions, N/Xe films were used to examine the effects of various environmental conditions.

FTIR analysis of the N/Xe BN films indicated that the films contained a majority (>50%) of the cubic phase of BN. Cross-sectional transmission electron microscopy (XTEM) analysis[16] was performed on other BN films deposited by IAPLD; this analysis revealed the presence of an interfacial region of amorphous and turbostratic BN (tBN) oriented with its basal planes perpendicular to the substrate/film interface. In the present work, it is assumed that the BN films are composed of cBN and sp^2-bonded BN. The role of this sp^2-bonded layer is not considered in the delamination process described in the following section. In addition, our stress calculations are performed with the assumption that the BN film is homogeneous in mechanical properties.

Films that were stored in the dry nitrogen and oxygen conditions showed no signs of delamination after more than two and three weeks, respectively. However, films stored in a saturated-water environment indicated initial signs of delamination within one day, and full delamination within 3 to 4 days of exposure. Films that were stored in dry-nitrogen environments for 12 days were removed and placed in a saturated water chamber; these films delaminated within 14 hours of exposure to high humidity. Films stored in dry oxygen for 22 days showed no signs of delamination. These films were removed and were also placed in the high-humidity chamber; delamination occurred within 24 hours thereafter. These experimental results clearly indicate that the humidity plays an important role in the delamination of the BN films.

The delamination of all the BN films exhibited ridge-type buckling[17] resulting from high compressive stresses. Figure 2 includes a series of optical and scanning electron microscope (SEM) micrographs showing examples of delaminated BN films. Because of the nonuniformity in film thicknesses, a highly accurate measurement of the film stress could not be established. However, film stresses were calculated as being in the 5 GPa ± 4 GPa range for BN films deposited under similar conditions. Due to film thickness uncertainties, there were no clear differences between stress values in the N/Ar, N/Kr and N/Xe films.

IV DISCUSSION

In our deposition process, there is an elliptical region where ion-irradiation occurs, surrounded by a non-irradiated region on the substrate (see Fig. 3). cBN is formed in the irradiated region while only sp^2-bonded BN forms elsewhere. In a separate paper[18] we have discussed the role of ion-irradiation on the formation of cBN. Examples of infrared spectra, shown in Figure 4, clearly indicate that the ion irradiation promotes the formation of cBN. Ion bombardment can promote compressive stresses in thin films[19]. The compressive stresses calculated for our BN films lie in the range of 2 to 9 GPa, consistent with stresses reported for cBN films deposited by other techniques[20,21]. Stress measurements on other BN films[21,22] have also indicated that the cubic BN films are typically under a relatively high compressive stress whereas the sp^2-bonded BN (or hBN/tBN) is at a much lower magnitude of stress. This is supported by the shift in the cBN IR absorption peak to larger wavenumbers, but nearly no shift in either IR reflectance peak associated with the hBN/tBN. A 25-cm^{-1} blue shift of the cBN IR peak indicates that the cBN is under a compressive stress of 6 to 7 GPa [23]. Thus it appears that our BN films consist of a compressively stressed cBN region surrounded by a low-stress sp^2-bonded BN region. This observation is consistent with that of Kester and Messier[22] for ion-assisted evaporated BN films. They also found that the cBN film regions had poor adhesion characteristics while the hBN regions showed no signs of delamination from the substrate. Figure 5 shows scanning electron micrographs indicating a delaminated cBN region and a hBN region adhered to the substrate. Compressive stress in the delaminated cBN film is indicated by the downward curling shown in the figure.

The total film stress, $\sigma_{f,\,tot}$, is often expressed as a summation of thermal and "intrinsic" stresses, i.e.,

$$\sigma_{f,\,tot} = \sigma_{th} + \sigma_{int} \;,$$

where σ_{th} is the thermal stress due to a difference in thermal expansion coefficients between the film and substrate, and σ_{int} is the intrinsic stress, which is related to the deposition process and the film's microstructure. If a biaxial stress state exists in the thin film, and the elastic modulus and Poisson's ratio of the film (E_f and ν_f, resp.) are known, then the thermal stress in the film may be calculated using the following relation:

$$\sigma_{th} = \frac{E_f}{(1 - \nu_f)} (\alpha_f - \alpha_s)\, \Delta T \;,$$

where α_f and α_s are the thermal expansion coefficients of the film and substrate, respectively, and ΔT is the temperature difference between the deposition and final (room) temperatures. Using bulk values of the coefficients of thermal expansion for silicon (2.9×10^{-6} °C^{-1})[24] and boron nitride (4.8×10^{-6} °C^{-1})[25], a typical ΔT value of 400°C, and an elastic modulus and Poisson's ratio for a randomly oriented polycrystalline aggregate of cBN[26] based on the elastic constants of Pesin[27], a tensile stresses of 710 MPa would result for cBN upon cooling to room temperature. Since the calculated stress in cBN is in the range of 2 to 9 GPa compressive stress, thermal stresses cannot be responsible for the large compressive stress, and therefore the intrinsic or microstructural stress is responsible for the large compressive BN film stress. Since the BN films do not delaminate immediately after deposition, the total film stress cannot alone exceed the stress required to delaminate the film from its substrate. Thus, some process must assist the delamination mechanism. A model is now presented that may explain this phenomenon.

Using a simple moment analysis, the stress induced in the substrate, σ_s, can be calculated by using the following relation:

$$\sigma_s = -4 \frac{t_f}{t_s} \sigma_f$$

where t_f and t_s are the film and substrate thickness, respectively, assuming homogeneous film stress distribution. We can assume that the maximum stress in the film occurs in the high-percentage cBN region, and has an average value of 5 GPa. The film thickness is approximately 50 nm, and the substrate thickness is 380 microns, thus a maximum tensile stress of approximately 10 MPa exists at the interface between the cBN and silicon substrate. Water vapor permeates through the BN film and then diffuses to the BN/Si interface to react with the interfacial material, resulting in the delamination. The large tensile stress in the substrate (induced by the film) exceeds the strength of the film interface, causing the fracture and subsequent delamination of the BN film. Hydrolized reaction products, a mixture of boron and silicon oxides, form at the interface. In the case of cBN, a comparatively lower density oxide results: the density of cBN is 3.45 g/cm^3 [25], whereas the density of B_2O_3 is in the range of 1.81 g/cm^3 (amorphous) to 2.46 g/cm^3 (crystalline) [28]. This change in density will further promote decohesion between the film and interface. That interfacial fracture and delamination is not observed in the hBN/tBN region of the film is probably because the stress in this film is considerably lower and because the densities of the tBN and hBN are substantially less; the density of hBN is 2.25 g/cm^3 [28] and the density of tBN is in the range of 1.80 to 2.23 g/cm^3 [29]

Since the films only delaminate in the presence of humidity, the chemical reactions that lead to BN film delamination, , are the aqueous oxidation of either BN or silicon. Exposure to dry oxygen does not reduce the time to delamination and so the oxidation is presumably electrolytic (i.e., akin to stress corrosion cracking in metals). Some of the relevant chemical reactions are listed in Table I, along free energies of formation (ΔG) for these reactions. It is well known that the oxidation of BN is facilitated by the presence of water.

In other words, it is suggested that the volume expansion (e.g., BN -> $(B_2O_3)_2(OH)$) at the interface is produced by a hydrolized species; for example, the reaction:

$$\frac{13}{2}O_2 + 8BN + H_2O = 2[(B_2O_3)_2(OH)] + 4N_2, \quad \Delta G = -445 \text{ kJ/mol}$$

is more likely to occur at room temperature than

$$2BN + \frac{3}{2}O_2 = B_2O_3, \quad \Delta G = -363 \text{ kJ/mol}$$

Therefore, it is likely that hydrolized species precede the formation of oxide compounds at the interface.

Since the water diffusion through the BN film is a necessary step in the delamination process, the microstructure of the BN film and the internal stress are important. Diffusivities are known to be influenced by stresses[30]. Previous studies[31] have shown that in ion-assisted deposited films, the stress varies with the ionic species . Therefore, the variation in the levels of film stress in our N/Ar, N/Kr and N/Xe BN films is most likely the rate controlling factor that is influencing the delamination times.

It has been previously reported that BN films reacts with water; Rand and Roberts[32] have previously demonstrated that hexagonal and amorphous BN films, deposited by a chemical vapor deposition (CVD) process involving diborane and ammonia, show signs of reactivity with water. They observed a weak IR absorption at 3430 cm^{-1} that they attributed to adsorbed water, and found that by exposing a BN film deposited on Si to a 2 hour exposure to 100°C steam, the thickness did not change significantly. They found that in general, BN films adhered to the substrates and were hydrophobic, and in some cases, small (0.1 mm) crystals of boric acid grew from a BN film after several months exposure to room atmosphere. This is somewhat consistent with our observation that the hBN/tBN regions in our films adhere well to the substrate and that the reaction products are contributing to the propagation of the cracks at the film interface.

Delamination of boron nitride films has been reported to be reduced by annealing[33], although no mechanism was discussed. It is likely that the annealing would not only reduce the diffusivity of the water through the film, but could also reduce the interfacial stresses, both of which would be expected to increase the delamination times. The lower compressive stresses in the BN film could conceivably reduce the tensile stresses below the fracture strength of the interfacial material, but additional experiments to determine what the contribution to the expansion of the propagating crack by the reaction products are necessary to determine this.

V CONCLUSION:

We can conclude from these experiments that moisture in the air is primarily responsible for the delamination of cBN films. cBN films stored in dry gas and under vacuum did not delaminate. BN films consisting of high-percentage cBN regions with adjacent, high-percentage sp^2-bonded BN regions, showed delamination only in the high-cBN areas. cBN films deposited with the heaviest (largest Z) ion irradiation delaminate in the shortest amount of time.

V ACKNOWLEDGMENTS:

Work done at Sandia was supported by the U.S. Department of Energy under contract DE-AC04-94AL8500 and in part by the Office of Basic Energy Sciences, Division of Materials Sciences.

Table I. Selected reaction products involving boron, nitrogen, oxygen, silicon and hydrogen.

substance	state[a]	ΔG (KJ/mol)	notes
SiO_2	cr	-856.64	α-quartz
	am	-850.70	
H_2SiO_3	ao	-1079.4	
H_4SiO_4	ao	-1316.6	
$H_2Si_2O_7$	ao	-1790.9	
B_2O_3	cr	-1193.4	
	am	-1182.3	
HB_4O_7	ao	-2719.9	
BN	cr	-228.4	

[a] Key to state abbreviations: cr: crystalline solid, am: amorphous solid, ao: aqueous solution, un-ionized substance, standard state, m = 1 mol/kg.

Reference: J. of Physical and Chemical Reference Data, Vol. 11, Suppl. No. 2, (1982).

Figure Captions:

Figure 1. Environmental chambers used for exposure of BN thin films to nitrogen or oxygen (left) or saturated water vapor (right).

Figure 2: Optical micrographs of delaminated N/Xe BN films as defined in the text. (a): exposed to dry oxygen, two weeks, (b) exposed to humid ambient, (c): exposed to dry nitrogen for 17 days and (d): exposed to high humidity for about 48 hours after removal from a 17-day nitrogen exposure.

Figure 3. Schematic representation of the sample geometry in side view (left) and top view (right). The film consists of a central, oval region (exposed to the ion-irradiation) that contains a large fraction of cBN, surrounded by an sp^2-bonded BN film.

Figure 4. Fourier transform infrared spectrum of a BN film. The spectrum indicates that a higher percentage of cBN exists in the ion-irradiated region, while the non-irradiated region is exclusively sp^2-bonded BN.

Figure 5: Scanning electron micrographs of BN films: (a), exposed to high-humidity, resulting in a delaminated region of high-percentage cBN (upper portion) and a fully-adhered region consisting primarily of sp^2-bonded BN; (b): exposed to high-humidity environment; compressive stresses causes downward curling once the film has delaminated.

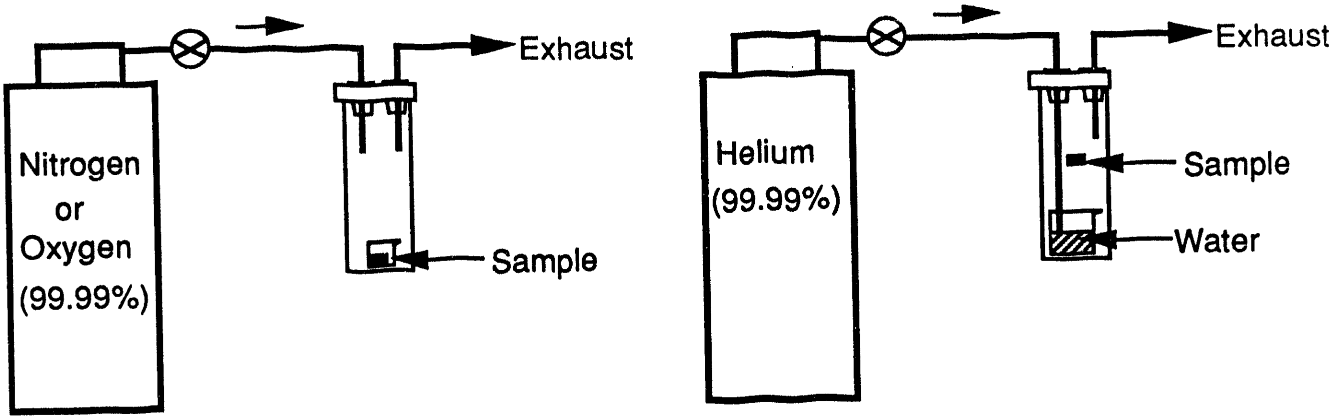
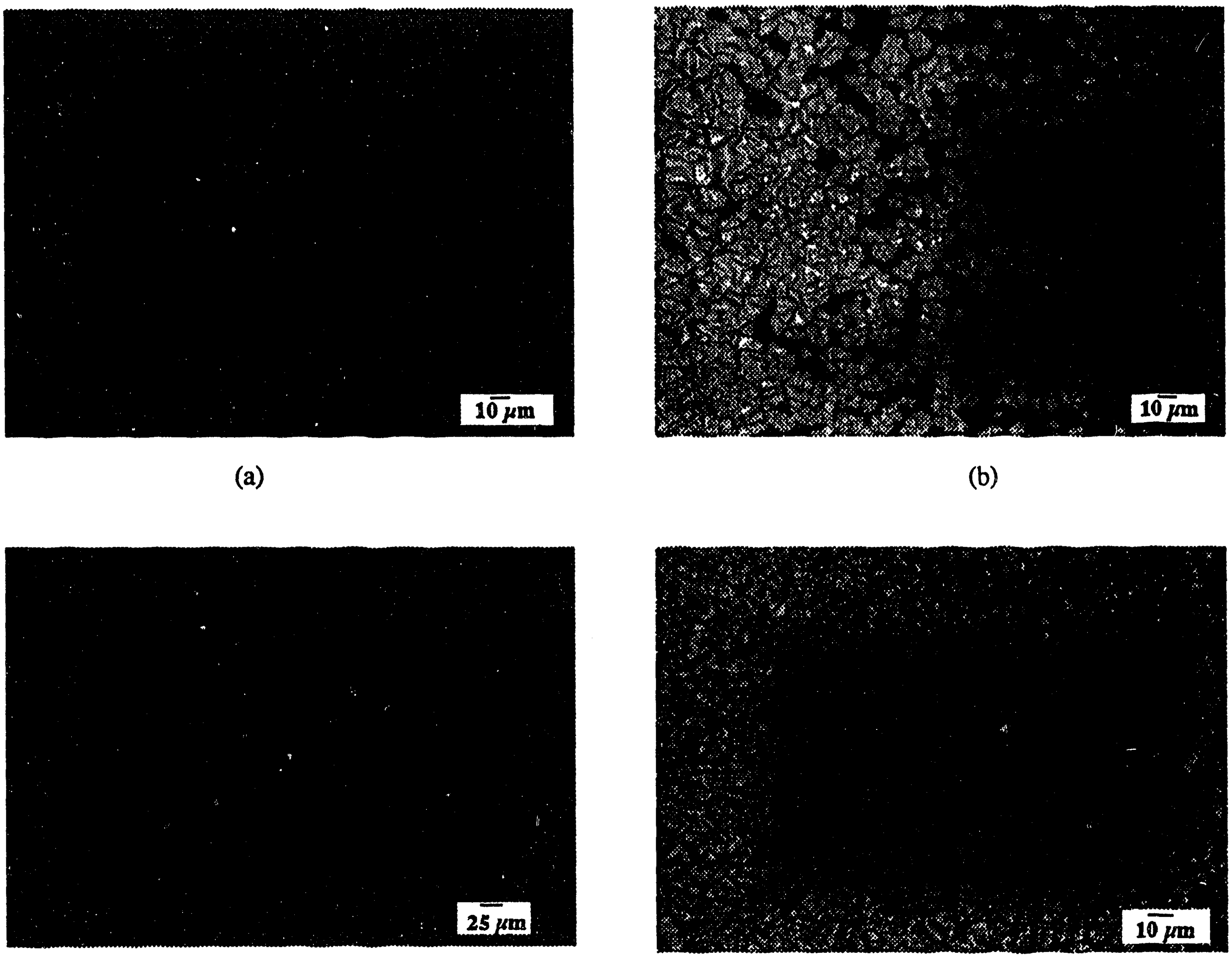

Nitrogen
or
Oxygen
(99.99%)
Exhaust
Sample
Helium
(99.99%)
Exhaust
Sample
Water

FIG. 1



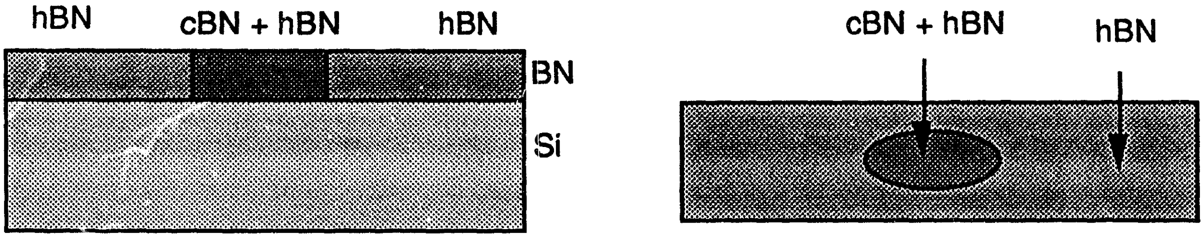
(a)

(b)

(c)

(d)

Figure 2: Optical micrographs of delaminated N/Xe BN films as defined in the text. (a): exposed to dry oxygen, two weeks, (b) exposed to humid ambient, (c): exposed to dry nitrogen for 17 days and (d): exposed to high humidity for nearly 48 hours after removal from a 17 day nitrogen exposure.



(side "view") (top "view")

FIG. 3

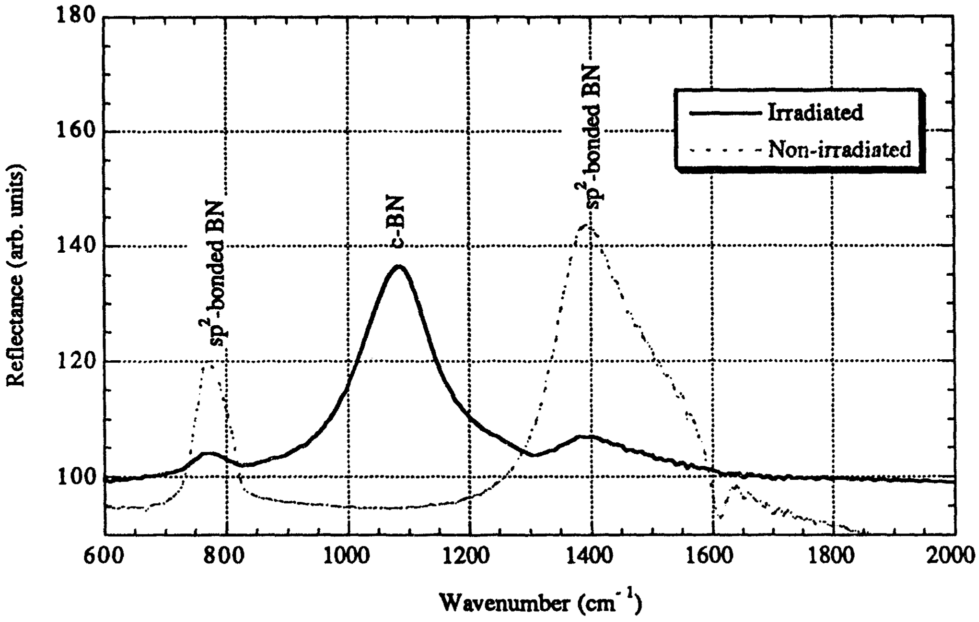
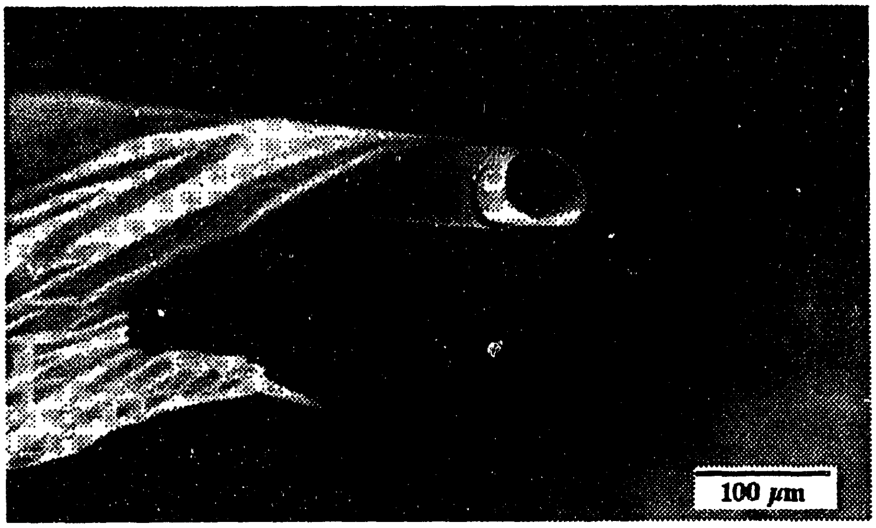

180
160
140
120
100
Reflectance (arb. units)
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm^{-1})
sp^2-bonded BN
c-BN
sp^2-bonded BN
Irradiated
Non-irradiated

FIG. 4

(a)



(b)

Figure 5: Scanning electron micrographs of BN films which were: (a), exposed to humid ambient, resulting in a delaminated region of high-percentage cBN (upper portion) and a fully-adhered region consisting primarily of hBN; (b): exposed to high humidity; compressive stresses in the BN films causes downward curling once the film has delaminated.

VI . REFERENCES:

1. S.P.S. Arya and A.D'Amico, Thin Solid Films, 157 (1988) 267.
2. W.Halverson and D.T. Quinto, J. Vac. Sci Technol. A 3(6) (1985) 2141.
3. S. Nishiyama, N. Kuatani, A. Ebe, and K. Ogata, Nucl. Instr. and Methods, B80/81 (1993) 1485.
4. N. Tanabe and M. Iwaki, Nucl. Instr. and Methods, B80/81 (1993) 1349.
5. T. Ikeda, Y. Kawate, and Y. Hirai, J. Vac. Sci. Technol. A, 8(4) (1990) 3168.
6. M. Okamoto, Y. Utsumi, and Y. Osaka, Jap. J. Appl. Physics, 29(6) (1990) L1004.
7. M. Okamoto, H. Yokoyama, and Y. Osaka, Jap. J. Appl. Physics, 29(5) (1990) 930.
8. S. Nishiyama, N. Kuratani, A. Ebe, and K. Ogata, Nucl. Instr. Meth. Phys. Res. B80/81 (1993)1485.
9. T.A. Friedmann, P.B. Mirkarimi, D.L. Medlin, K.F. McCarty, E.J. Klaus, D. Boehme, H.A. Johnsen, M.J. Mills, and D.K. Ottesen, J. Appl. Phys., *in press*, (1994).
10. T.A. Friedmann, W.M. Clift, H.A. Johnsen, E.J. Klaus, K.F. McCarty, D.L. Medlin, M.J. Mills and D.K. Ottesen in D. Braren, J.J. Dubowski, and D.P. Notrton (eds.) Laser Ablation in Materials Processing: Fundamentals and Applications, , Vol 285, Pittsburgh, PA: Materials Research Society, 1993, p. 507.
11. R. Geick, C.H. Perry and G. Rupprecht, Phys. Rev. 146 (1966) 543.
12. P.J. Gielisse, S.S. Mitra, J.N. Plendl, R.D. Griggis, L.C. Mansur, R. Marshall and E.A. Pascoe, Phys. Rev. 155 (1967)1039.
13. G. Stoney, Proc. R. Soc. London Ser. A, A82 (1909) 172.
14. B.S. Berry and W.C. Pritchet, J. Appl. Phys., 67 (1990) 3661.
15. W.A. Brantley, J. Appl. Phys., 44 (1973) 543.
16. D.L. Medlin, T.A. Friedman, P.B. Mirkarimi, P. Rez, and K.F. McCarty, submitted to xxxx.
17. A. Borer, R. Derby and I. May, in J.C. Bravman, W.D. Nix, D.M. Barnett, and D.A. Smith (eds.) Thin Films: Stresses and Mechanical Properties, Materials Res. Soc. Press, Pittsburgh, PA, 1989, p. 231.
18. P.B. Mirkarimi, K.F. McCarty, D.L. Medlin, W.G. Wolfer, T.A. Friedmann, E.J. Klaus, G.F. Cardinale and D.G. Howitt, (*submitted to Journal of Materials Research*), 1994.
19. D.W. Hoffman and M.R. Gaerttner, J. Vac. Sci. Technol. 17 (1980) 425.

---

20. D.R. McKenzie, W.D. McFall, W.G. Sainty, C.A. Cavis, and R.E. Collins, Dia. and Rel. Materials, 2 (1993) 970.

21. T. Ikeda, Y. Kawate and Y. Hirai, J. Vac. Sci. Technol. A, 8 (4) (1990) 3168,.

22. D.J. Kester and R. Messier, J. Appl. Phys. 72 (2) (1992) 504.

23. The increase in wavenumber of the cBN reflectance peak from 1065 cm-1 to approximately 1090 cm-1 can be described by a mode Grüneissen parameter. Calculations indicate that such a shift can be induced by compressive stresses in the range of 6 to 7 GPa.

24. P. Klocek, L.E. Stork, M.W. Boucher, C. DeMilo, SPIE Proceedings, Vol. 929, Infrared Optical Materials VI (1988) 69 .

25. R.C. DeVries, *Cubic Boron Nitride: Handbook of Properties*, Report. #72CRD178, 1972 (General Electric Co.).

26. G.F. Cardinale, *unpublished*,1994.

27. V.A. Pesin, Sverkhtverdye Materialy, 4 (1984) 30.

28. D. R. Lide, ed. CRC Handbook of Chemistry and Physiscs, 74th edn., CRC Press, 1994.

29. L. Duclaux, B. Nysten, J-P. Issi, and A.W. Moore, Phys. Rev. B, 46 (6) (1992) 3362.

30. D. Gupta and P. S. Ho., eds., Diffusion phenomena in thin films and microelectronic materials, Noyes Publications, Park Ridge, N.J., (1988).

31. H. Windischmann, J. Appl. Phys., 62 (5) (1987) 1800.

32. M.J. Rand and J.F. Roberts, J. Electrochem. Soc: Sol. St. Sci., 115 (4) (1968) 423.

33. D.J. Kester, K.S. Ailey, R.F. Davis, and K.L. More, J. Mater. Res. 8 (6) (1993) 1213.

DATE
FILMED
10/5/94

END