

UCRL-JC-123992

CONF-960753--/

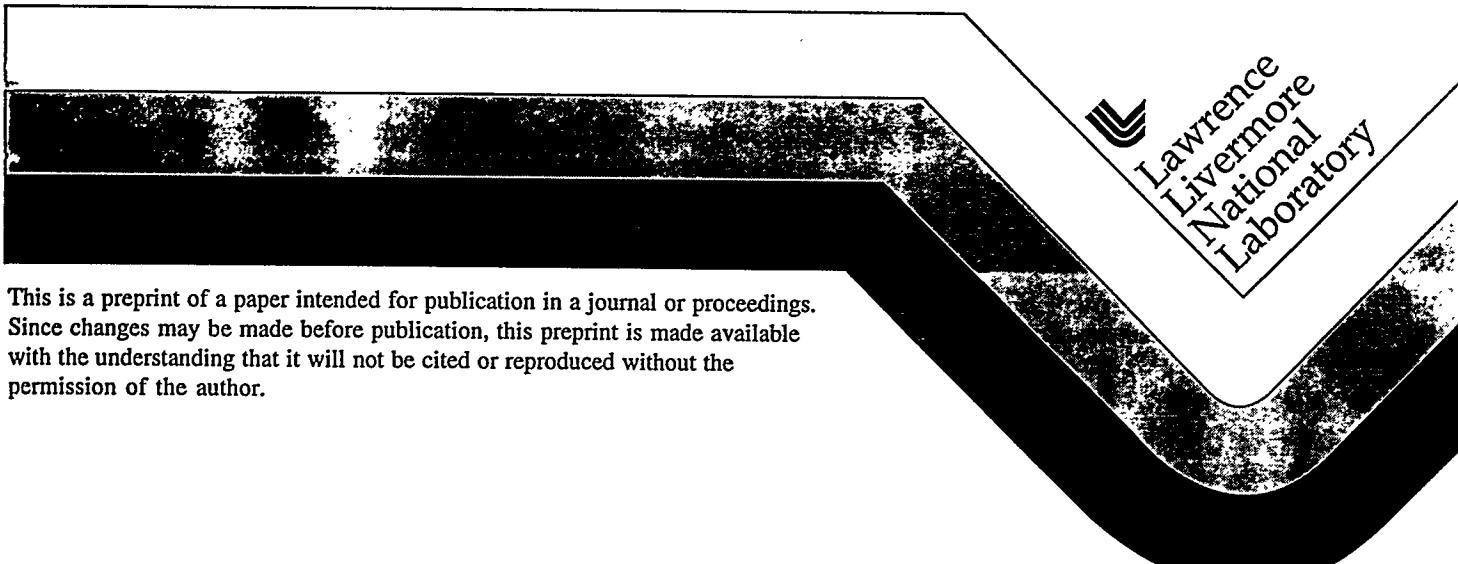
Properties of Boron/Boron-Nitride Multilayers

Alan F. Jankowski
Mark A. Wall
Jeffrey P. Hayes
Kathleen B. Alexander*

*Oak Ridge National Laboratory

This paper was prepared for submittal to the
Third International Conference on Nanostructure Materials
Kona, HI
July 7-12, 1996

June 1996



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

PROPERTIES OF BORON/BORON-NITRIDE MULTILAYERS

Alan F. Jankowski, Mark A. Wall, Jeffrey P. Hayes
University of California - Lawrence Livermore National Laboratory
Department of Chemistry & Materials Science, Livermore, CA 94550 USA

Kathleen B. Alexander
Martin Marietta Energy Systems - Oak Ridge National Laboratory
Metals and Ceramics Division, Oak Ridge, TN 37831 USA

Abstract -- Boron-Nitride films are of interest for their high hardness and wear resistant properties. Large intrinsic stresses and poor adhesion which often accompany high hardness materials can be moderated through the use of a layered structure. Alternate layers of boron (B) and boron-nitride (BN) are formed by modulating the composition of the sputter gas during deposition from a pure B target. The thin films are characterized with transmission electron microscopy to evaluate the microstructure and with nanoindentation to determine hardness. Layer pair spacing and continuity effects on hardness are evaluated for the B/BN films.

INTRODUCTION

Vapor deposition techniques have been developed to deposit boron (B) and boron nitride (BN) films. The growth of pure boron and cubic boron nitride (cBN) are pursued for high hardness applications. Formation of the cubic phase when depositing from hexagonal boron nitride (hBN) targets has been achieved through the use of very energetic processes.(1-4) An application of high voltage, bias sputtering or ion beam bombardment at the substrate is required which then produces large residual stresses within the films. A less energetic deposition process would be desireable. Alternatively, the use of a multilayered structure could take advantage of the high hardness property without the formation of large residual stresses.(5)

A measurement technique to assess a multilayer application for protective hard coatings is nanoindentation. To determine the hardness of submicron thick coatings requires control of indentation depths to <10 nm.(6,7) An observation that dislocation mobility should be inhibited by the composition modulation when combined with layers small enough to cease dislocation generation mechanisms within a given layer implies that the multilayer strength and hardness should increase for decreasing modulation wavelength λ .(8,9) An enhancement of micro-hardness was measured for single crystal TiN/VN(100) superlattices prepared by reactive magnetron sputtering.(10) A 75% increase was observed for λ decreasing from 32 to 7.5nm, at which point the hardness increased an additional 75% as the λ decreased to 5nm. Below 5nm, the hardness enhancement abated to rule-of-mixtures values. The hardness of $(\text{TiN})_{.7}/(\text{NiCr})_{.3}$ multilayers sputter deposited onto tool steels were assessed using an ultra-microindentation system where the penetration depth of the indenter was <10% of the film thickness.(11) The hardness increased to a maximum 60% above the rule-of-mixtures value as λ decreased to 1.2nm. The enhancement of hardness in multilayers is not always large as is often the case for strained layered superlattice structures.(12) For example, only a 10% increase is measured

Table 1. B, BN and B/BN Multilayer Film Samples

Sample	Substrate	t (μm)	N	λ (nm)	H (GPa)
B	Ni/Silicon	0.14	-	-	27.0
B/BN	Sapphire	0.15	20	7.5	8.5
B/BN	Sapphire	0.17	67	2.5	4.0
B/BN	Ni/Silicon	0.15	20	7.5	1.4
B/BN	Ni/Silicon	0.16	40	4.0	1.1
B/BN	Ni/Silicon	0.17	100	1.7	1.0
BN	Ni/Silicon	0.26	-	-	0.2

above the rule-of-mixtures value for Cu/Cr laminates.(13) Therefore, although the B/BN structures are not anticipated to form a multilayer superlattice, the use of nanometric $\lambda(s)$ may create a hardness at least equivalent to a rule-of-mixtures value in an adherent coating.

EXPERIMENTS AND RESULTS

Synthesis Method

The recent development of fully dense, pure B targets has made it possible to initiate an investigation of B and BN deposition without the presence of precursor compounds.(14-16) In addition to investigating B and BN films, multilayer structures will be synthesized that consist of a hard B layer alternating with a compliant BN layer. The compliant layer may moderate residual stresses formed within the hard layer. The synthesis of the B film proceeds from the rf sputter deposition of the B target using an unbalanced planar magnetron.(15-17) The deposition chamber is cryogenically pumped to a base pressure of 5.3×10^{-6} Pa in 12 hrs including a 4 hr, 100 °C bake out. Sapphire and 20-50nm Ni-coated silicon wafers are used as the substrates which are horizontally positioned 9 cm away from the center of the 6.4cm diameter B target. The substrate temperature of 215 ± 10 °C is controlled using a Boralectric™ heater. The sputter gas pressure is nominally selected as 1 Pa (7 mTorr) with a constant flow rate of 28 cc/min. The deposition rate is monitored with a calibrated 6 MHz Au-coated quartz crystal. An increase in forward power from 100 to 300 W produces a linear increase in deposition rate from 0.007 to 0.021 nm/s. The multilayer synthesis proceeds by cycling the gas flow composition between Ar and Ar-25%N₂ to produce N layer pairs. A 200 W forward power is used to produce a 0.15-0.16 μm total film thickness t . The low deposition rate combined with the 15-20 sec time interval needed to stabilize the flow rate yields an interfacial width of <0.3 nm. The samples prepared for nanoindentation examination are listed in Table 1.

Microstructure Characterization

Composition analysis using Auger electron spectroscopy coupled with depth profiling shows the BN deposits have a 4:5 B to N ratio.(17) Two methods used to examine the structure of the multilayers are $\theta/2\theta$ mode x-ray diffraction (XRD) and transmission electron microscopy (TEM). Bright field (BF) imaging of the films prepared in cross-section and selected area diffraction (SAD) provide an analysis of the growth morphology, film texture and crystal structure. BF images near the defocus condition reveal the B/BN layered structure (Fig. 1). The 20 layer pair structures have a measured $\lambda = 7.5$ nm in the growth direction (indicated by

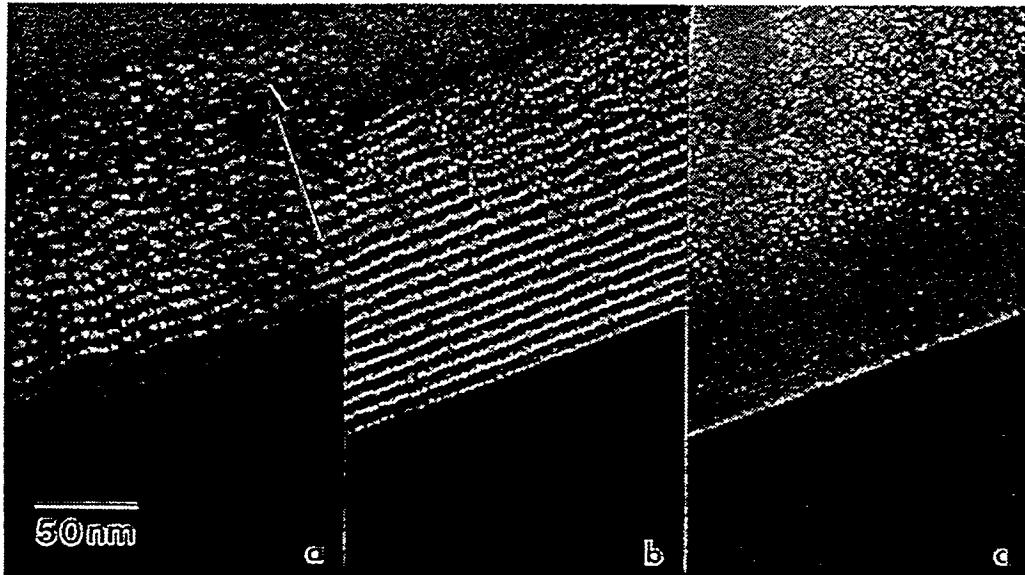


Fig. 1 - Bright field images of the 20 layer pair B/BN films as viewed in cross-section on the (a) Ni/Si and (b) sapphire substrates as well as the (c) 67 layer pair B/BN film on sapphire.

the arrow). The layers are of equal thickness and conformal to the substrate surface. Whereas the layering is initially continuous, the roughness introduced by the Ni/Si substrate surface results in a diffuse appearance (Fig. 1a) to the final layers. Likewise, mixing is apparent in the final layer pairs (Fig. 1c) of the 2.5nm B/BN film. Minimum crystallographic information is obtained using XRD and SAD for the B, BN and B/BN films. The diffraction results indicate that the B film appears to be amorphous whereas both the BN and B/BN multilayer films have diffuse SAD ring patterns with interplanar spacings that best fit a disordered hBN phase.(17)

Hardness Measurement

Nanoindentation load vs displacement measurements have been developed to determine the hardness H of submicron thick coatings.(6) A NanoIndenter is used to produce arrays of six indentations at each of several depths. Typically, the indenter is loaded at a velocity of 3-6 nm/s, held at peak load until the velocity decreases below 0.1 nm/s, and then unloaded at a constant rate. Loads are measureable above 0.25 μ N and indentation depths to within 0.3 nm. The hardness is equivalent to the peak indentation load divided by the projected contact area of the indenter impression. The contact area is proportional to the square of the indentation depth. The indentation depth is determined by extrapolating the initial 25% of the unloading curve to zero load using a least squares fit of a straight line. The determination of contact area through an effective contact depth d is generally more accurate than using either the indentation depth at peak load or the final depth. Limitations to the assumptions of linear unloading and the shape approximation for the indenter tip can affect the measured hardness values by 10-15%.(7)

A variation in the hardness measured for a single film will occur with different indentation depths.(18) At some critical indentation depth, the substrate will influence the measured film hardness. A technique for determining the critical depth is based on the well-known Meyer relation.(19) For bulk materials, a logarithmic plot of applied load versus the

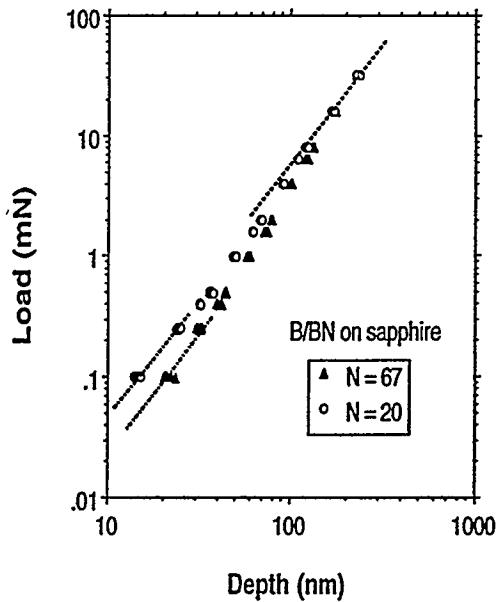


Fig. 2 - Meyer plots of the nanoindentation data for the B/BN multilayers on sapphire.

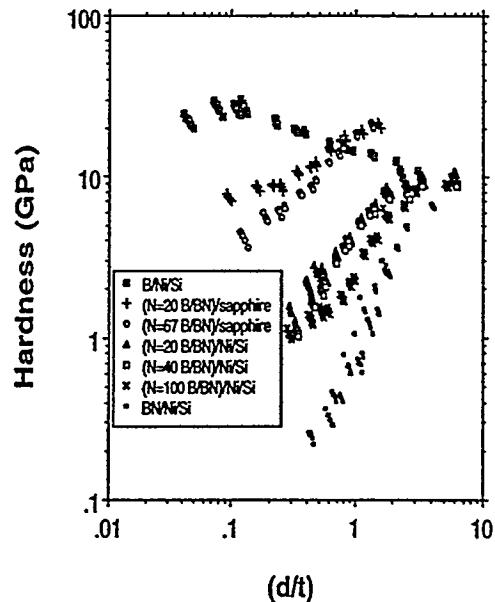


Fig. 3 - A plot of nanoindentation Hardness versus (d/t) for each sample listed in Table 1.

indentation diagonal generally produces a straight line. Deviation from the straight line occurs at the depth where the substrate begins to influence the indentation of the thin film coating.(20) Hardness values determined below the critical indentation depth will be representative of only the coating. The critical indentation depth should be determined from Meyer plots for multilayer structures since the hardness may vary as a function of λ . In this analysis, Meyer plots will be constructed using load as a function of d , since the contact depth is directly proportional to the indentation diagonal.

The Meyer plots for the B/BN multilayer coatings clearly show (Fig. 2) the transition from indenting only the film to measuring the hardness contribution of the sapphire substrate. Each load curve deviates away from the tangent to the film as the indentation depths increase above 30 nm. A continuous change in hardness is measured as (d/t) increases to 1 (Fig. 3) beyond which the curves converge on the substrate hardness (21GPa for sapphire and 10 GPa for Ni/Si). Therefore, the measured hardness of the B/BN coatings are found at the shallow indentation depths and are listed in Table 1, accordingly. These results follow the ASTM recommendation to measure the coating hardness at $d/t < 0.1$.(21)

DISCUSSION AND SUMMARY

The measured hardness of the B/BN multilayers is found to decrease for $\lambda < 7.5$ nm. This result can be directly attributed to the mixing between the B and BN layers as apparent in the TEM cross-section images. The intermixing of layers is especially pronounced for substrates with rougher surfaces as evidenced by comparing the hardness values for the N=20, 7.5 nm layer pair samples. In fact, the N=67, 2.5nm layer pair sample deposited on sapphire is smoother and harder than the N=20, 7.5nm layer pair B/BN deposited on Ni/Si.

Nanoindentation is used to measure the hardness of coatings less than $0.2\mu\text{m}$ thick. Hard coatings of B which are subject to stress-induced delamination from the substrates are produced by sputter deposition from a pure B target. Soft hBN films are reactively sputter deposited using a B target with an Ar-N₂ working gas mixture. Multilayers of B and BN are deposited by modulating the sputter gas composition between Ar and Ar-N₂, respectively. Intermixing of layers during deposition is accentuated for substrates with greater surface roughness. There is no apparent hardness enhancement in the B/BN coatings as superlattice effects are not present in these multilayers.(12) A near rule-of-mixtures hardness is obtained for adherent coatings on sapphire wherein the B/BN layering is smooth and continuous.

ACKNOWLEDGMENTS

This work is supported by the Basic Energy Sciences - Synthesis and Processing Center for Hard Surfaces and was performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory under contract #W-7405-Eng-48 and by Oak Ridge National Laboratory under contract #DE-AC05-84OR21400.

REFERENCES

1. D. Kester, K. Alley, D. Lichtenwainer and R. Davis, *J. Vac. Sci. Technol. A* 12, 3074 (1994).
2. T. Friedmann, et al., *J. Appl. Phys.* 76, 3088 (1994).
3. T. Wada, and N. Yamashita, *J. Vac. Sci. Technol. A* 10, 515 (1992).
4. N. Tanabe, T. Hayashi and M. Iwaki, *Diamond Relat. Mater.* 1, 883 (1992).
5. S. Barnett and M. Shinn, *Ann. Rev. Mater. Sci.* 24, 481 (1994).
6. M. Doerner and W. Nix, *J. Mater. Res.* 1, 601 (1986).
7. W. Oliver and G. Pharr, *J. Mater. Res.* 7, 1564 (1992).
8. J. Koehler, *Phys. Rev. B* 2, 547 (1970).
9. L. Palatnik, A. Il'inskii and N. Sapegin, *Sov. Phys. Sol. Stat.* 8, 2016 (1967).
10. U. Helmersson, et al., *J. Appl. Phys.* 62, 481 (1987).
11. X. Chu, M. Wong, W. Sproul and S. Barnett, *Surf. Coatings Technol.* 61, 251 (1993).
12. A.F. Jankowski, *NanoStruct. Mater.* 6, 179 (1995).
13. R.F. Bunshah, R. Nimmagadda, H.J. Doerr, B.A. Movchan, N.I. Grechanuk and G.G. Didkin, *Thin Solid Films* 112, 227 (1984).
14. D. Makowiecki, A. Jankowski, M. McKernan and R. Foreman, *J. Vac. Sci. Technol. A* 8, 3910 (1990).
15. M. McKernan, D. Makowiecki, P. Ramsey and A. Jankowski, *Surf. Coatings Technol.* 49, 411 (1991).
16. D. Makowiecki and M. McKernan, *Fabrication of Boron Sputter Targets*, U.S. Patent No. 5,392,981 (February 28, 1995).
17. A. Jankowski, J. Hayes, M. McKernan and D. Makowiecki, Lawrence Livermore National Laboratory UCRL-JC-121985 (1995).
18. B.D. Fabes, W.C. Oliver, R.A. McKee and F.J. Walker, *J. Mater. Res.* 7, 3056 (1992).
19. G.F. Van der Voort, *Metallography Principles and Practice*, McGraw-Hill, New York (1984).
20. C. Feldman, F. Ordway and J. Bernstein, *J. Vac. Sci. Technol. A* 8, 117 (1990).
21. ASTM Standard E 92, *Annual Book of Standards 3.01*, p. 264, American Society for Testing and Materials, Philadelphia (1987).