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ABSTRACT

Boron-nitride (BN) films are deposited by the reactive sputter deposition of fully dense, boron targets utilizing a planar magnetron source and an argon-nitrogen working gas mixture. Near-edge x-ray absorption fine structure analysis reveals distinguishing feaures of chemical bonding within the boron 1s photoabsorption cross-section. The hardness of the BN film surface is measured using nanoindentation. The sputter deposition conditions as well as the post-deposition treatments of annealing and nitrogen-ion implantation effect the chemical bonding and the film hardness. A model is proposed to quantify the film hardness using the relative peak intensities of the π*-resonances to the boron 1s spectra.

Keywords: boron-nitride
chemical bonding
hardness
reactive sputtering
x-ray absorption

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I. INTRODUCTION

Boron and its nitride coatings are of interest for electronics, optical filters, wear resistance and high hardness applications. The hardness of crystalline films can be related to the microstructure. The hardness of multilayer films can be dependent on superlattice features, e.g., the mobility of dislocations is effected by the difference between layer elastic constants, interfacial widths and spacings.[1-2] Layer spacing effects on hardness alone are analogous to classic Hall-Petch behavior.[3] However, in general, hardness may be thought of as an intrinsic property determined by the chemical bonding within the material. Near-edge x-ray absorption fine structure (NEXAFS) analysis can be used to identify the exact nature of chemical bonding in a material. For elemental boron and boron-nitride (BN) phases, the features of chemical bonding are shown to broadly correlate with the hardness of crystalline, nanocrystalline, and amorphous films.[4-7] Curve fitting of the NEXAFS spectra beyond the σ^*-edge is used to determine the relative sp^2 and sp^3 intensities that provides a quantification of the phase content.[5-6] An increase in hardness is found with an increase in the cubic boron-nitride (cBN) phase content for sputter deposited films.[6]

The effects of sputter gas pressure, flow and composition along with substrate temperature and applied bias are assessed on the formation of crystalline phases in BN films deposited by rf sputtering pure boron targets using unbalanced planar magnetrons.[6-7] Hardness can be influenced by post-deposition treatments as well. Ion implantation of hexagonal boron nitride (hBN) with N_2^+ was shown with NEXAFS to induce a significant proportion of sp^3 bonding characteristic of cBN.[4] A 100-fold variation in hardness appears for BN films that can be characterized in entirety by sp^2 bonding features alone.[7] The presence of defects in the chemical bonding of hBN appear as resonances found beyond the π^*-edge.[4-5] It is the present objective to develop a model to quantify the hardness of films composed of elemental B and the hBN phase using the π^* resonance intensities in the NEXAFS spectra. This approach suggests that hardness can be considered an intrinsic material property.

II. EXPERIMENTAL METHOD

The 0.2µm thick films are prepared by the sputter depostion of pure boron using planar magnetrons operated in the rf mode.[6-8] Synthesis of the boron sputter targets is described in detail elsewhere.[9] The deposition chamber is cryogenically pumped to a 5.3×10^{-6} Pa base pressure. The elemental B films are deposited using Ar as the sputter gas.[8] The BN films are deposited using a reactive Ar-50% N_2 gas mixture.[6] The layered B/BN samples are deposited by cycling the sputter gas between Ar and the Ar-N_2 mixture.[7] In addition to enhancing coating adherence, a Ni epilayer is reported to enhance epitaxial crystalline growth.[10-11] All samples are deposited on Si wafers sputter coated with 20-50nm of Ni. $Cu\ K\alpha$ x-ray diffraction in the $\Theta/2\Theta$ mode reveals a textured deposit of Ni(111). The substrate is horizontally positioned 9 cm from the center of the 6.4cm diameter target. A substrate temperature of 300˚C is controlled using a Boralectric™ heater. The sputter gas pressure is less than 1 Pa using a 28 cc min^{-1} flow rate. A deposition rate of 7×10^{-5} nm W^{-1} s^{-1} is monitored with calibrated 6 MHz Au-coated quartz crystals.

The boron and nitride films are characterized using near edge x-ray absorption fine structure (NEXAFS) spectroscopy.[4-5] Unique spectral features in the boron and nitrogen 1*s* photoabsorption cross sections correspond with resonances that are specific to discrete BN phases.[12] The photon energy of monochromatic synchrotron radiation is scanned through the core-level edge while monitoring the electron yield to measure the B 1*s* core-level photoabsorption cross-section. The low-energy, long mean-free-path electron emission dominates the signal yielding a bulk sensitive measurement. The transition of 1*s* initial states into p-like empty final states is associated with sp^2 hybridized, planar bonding that is characteristic of hBN and appears as the narrow, intense transition at 192 eV. This π^* resonance is absent in sp^3 tetrahedrally bonded materials as cBN which uniquely evidence an absorption maximum step into σ^* continuum states above 194 eV. The resonance peak at 192 eV is indicative of B-(N_3) bonding in hBN. The presence of N-void defects in the hBN structure are representative of B-(BN_2) and B-(B_2N) corresponding to the successive satellite peaks above

192 eV.[4, 13] The diffuse *peak* for elemental boron at 194 eV can be correlated with some degree of planarization of *sp*^{3} tetrahedral bonding, similar in signature to the sub-surface boron layer that forms in silicon.[14]

Prior analysis of composition using Auger electron spectroscopy and crystal structure using transmission electron microscopy indicate the pure boron films are amorphous.[8] The BN films are a distorted hexagonal phase with 53 ± 2 atomic percent nitrogen.[6] The B/BN sample(s) consist of layers of equal thickness that compose a 7.5 nm repeat spacing.[7] The metastability of the BN and B/BN films is assessed using two different post-deposition treatments. The layered B/BN sample is annealed in vacuum at 450 ˚C for 1 hr. The BN samples are subjected to N^+ ion implantation conducted at 90 keV and 180 keV. A total fluence of 10^{17} cm^{-2} is delivered using a beam current density of 88 ± 5 μA cm^{-2}.

The hardness of the submicron thick films is measured with a Nanoindenter™. A three-sided pyramid (Berkovich indenter) is used to produce indentation arrays at each of several depths. Loads are measureable above 0.25 μN and indentation depths to within 0.3 nm. In practice, the film hardness should be determined at the most shallow indentations as the substrate will influence the measured hardness.[15] The analysis of load-displacement curves as developed for bulk homogeneous materials has evolved to better define parameters such as true contact area which are used in the detemination of hardness for stiff materials as well as inhomogeneous systems.[16-17] Although there are limitations imposed by analizing inhomogeneous and hard materials as BN, the coating-substrate hardness is determined using the method proposed by Oliver and Pharr.[18-19]

III. EXPERIMENTAL RESULTS & ANALYSIS

The B 1*s* photoabsorption cross section to the NEXAFS spectra (Fig. 1) of pure boron and the as-deposited (i.e. unimplanted) BN films contain the π*-resonance features as reported between the photon energies of 192 and 194 eV.[4-5] The spectra for the B/BN layered sample

(Fig. 1) appears as a superposition of the curves for the pure boron and unimplanted BN samples[7] The effect of N^+ ion irradiation is seen (Fig. 1) for the 90 keV implant condition as the intensity of the N-void defect peaks increase in comparison to the unimplanted condition[13] The spectra for the 180 keV implant condition (not shown) evidences a very small decrease in the N-void defect peak intensities relative to the unimplanted condition. The spectra of the annealed B/BN sample (not shown) evidences a decrease in the N-void defect intensities relative to the as-deposited condition. The peak intensities (**I**) of the B 1s spectra are quantified for each BN bonding vaiant. A fitting procedure is applied to deconvolute the π* resonance peaks into a superposition of four Gaussian curves.[4, 7] Present results using this fitting procedure are listed in Table 1 for each sample.

The hardness measured for each sample (Fig. 2) increases with the indenter depth. The hardness of each sample converges on 9-10 GPa, the value of the Si substrate, beyond a penetration equal to the film thickness. To measure the film hardness requires consideration of only the most shallow indentation depths, ideally those indents less than 10% of the film thickness, i.e. 20 nm for these samples.[15] The average experimental hardness ($\mathbf{H_e}$) values for each sample are listed in Table 1. The hardest sample is the pure boron film whereas the softest is the 180 keV implant condition of the BN sample. The hardness of an unimplanted region of both the 90 and 180 keV irradiated BN samples are equal (as should be expected). The 90 keV implant sample evidences an increase in hardness compared to the unimplanted condition as opposed to the change due to the 180 keV implant. The layered B/BN sample has a hardness intermediate to the pure B and unimplanted BN samples. The annealed B/BN film evidences a decrease in hardness as listed in Table 1.

In general, the relative hardness of each sample corresponds with the relative peak intensities of the π* resonances. The hardest films have a strong (elemental B) peak intensity at 194 eV whereas the softest films have a strong 192 eV peak, i.e. primarily B-(N_3) bonding. An empirical model takes the approach to directly relate the relative peak intensities to the film hardness. The modeled value for hardness ($\mathbf{H_m}$) can be computed from an eigenvalue set for which each hardness H(i) corresponds to a unique peak of the π* resonance. The H(i) value will increase corresponding to an increase in the bond strength. The modeled hardness ($\mathbf{H_m}$) is the sum of the relative peak intensity **I**(i) multiplied by the intrinsic hardness H(i), that is

$$\mathbf{H_m} = \sum_{i} H(i) \bullet \mathbf{I}(i) \qquad (1)$$

The following eigenvalues are numerically determined by best fitting H(i) to the set of experimental values for **I**(i) and Hardness, i.e. the condition $\mathbf{H_m} = \mathbf{H_e}$.

$$H(B\text{-}N_3) = 0.10 \text{ GPa} \qquad (2a)$$

$$H(B\text{-}BN_2) = 0.50 \text{ GPa} \qquad (2b)$$

$$H(B\text{-}B_2N) = 2.5 \text{ GPa} \qquad (2c)$$

$$H(B) = 28 \text{ GPa} \qquad (2d)$$

The modeled Hardness ($\mathbf{H_m}$) for each sample is listed in Table 1. The experimental and modeled values quantitatively match very well over a range exceeding two-orders of magnitude, as indicated by the 0.986 correlation coefficient (R^2) to a linear curve fit of $\mathbf{H_m}$.versus $\mathbf{H_e}$.

IV. DISCUSSION

Stabilization of the cBN phase in thin films can be achieved through the use of ion-assisted deposition techniques, e.g. high voltage, bias sputtering or ion beam bombardment at the substrate.[**20-23**] Mechanisms proposed for cBN stabilization in BN films include both preferential sputtering effects [**24**], the presence of large stresses [**25-26**] and subplantation [**27-28**] wherein low energy ions are implanted below the surface to increase local density. Post deposition treatments of hBN are also revealing, as 180 keV N_2^+ (i.e. a condition eqivalent to 90 keV N^+) ion implantation at a 10 µA cm^{-2} current density induced a significant proportion of *sp*^{3} bonding characteristic of cBN.[**4**] Whereas N-void defect introduction to the BN film is evident in the π*-resonances, there are no noticeable changes in the B 1*s* spectra beyond the σ*-edge indicative of sp^3 bonding at the higher (88 μA cm^{-2}) current density used in this study. Therefore, an ion current threshold is clearly evident. A higher energy (180 keV N^+) ion implant at the greater current density, as is the case for the heat treatment, effectively anneal out the N-void defect structure hence decrease the film hardness. Thus, examination with core level photoabsorption to study BN defects and metastable bonding configurations confirms that the presence of point defects support mechanisms that involve defect creation in cBN formation.[**4-5**] Recently, similar findings requiring defect generation are found in the mass and energy measurement of species responsible for cBN growth in rf bias sputter conditions.[**29-30**]

V. SUMMARY

Boron, BN, and layered B/BN films are sputter deposited from pure boron targets at low tempertaure onto Ni-coated Si substrates. For the set of deposition conditions examined, the films are found to be composed of a mixture of amorphous boron and a defected hexagonal phase as characterized using NEXAFS.[**4**] The as-deposited structure and chemical bonding are metastable. Either heat treatment or N^+ ion implantation (at high energy and high current density) can anneal out defects (as N-voids) and soften the film. Conversely, at lower N^+ implantation energy (e.g. 90 keV), irradiation of the BN samples creates additional defects (as N-voids) which harden the film. It appears that an energy range exists requiring defect creation for which the BN films harden. This result is similar to the findings of ion-beam assisted deposition and ion implantation studies for the stabilization of cBN during growth.[**4-5, 27-28**] It is shown possible to develop a self-consistent model that can be used to quantify the surface hardness based on the chemical bonding of the film. A hardness value intrinsic to each bonding configuration within the π* resonance is numerically fitted from the B 1s spectra and experimental hardness measurements.

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Table 1. Boron, layered B/BN, and N^+ implanted samples

Sample	**I** (B-N_3)	**I** (B-BN_2)	**I** (B-B_2N)	**I** (B)	$\mathbf{H_e}$ (GPa)	$\mathbf{H_m}$ (GPa)
pure Boron	0.00	0.01	0.03	0.96	26.4 ± 2.4	27.0
layered B/BN	0.22	0.18	0.16	0.44	15.6 ± 0.2	12.8
heated B/BN	0.19	0.30	0.26	0.25	8.38 ± 0.64	7.82
90 keV implant	0.43	0.28	0.18	0.11	3.41 ± 0.52	3.67
unimplanted BN	0.81	0.13	0.05	0.01	0.86 ± 0.04	0.55
180 keV implant	0.92	0.06	0.02	0.00	0.14 ± 0.01	0.17

FIGURE CAPTIONS

Fig. 1 The electron yield intensity (arb. un.) variation with photon energy (eV) in the near-edge x-ray absorption fine structure B 1s spectra for the B, BN, layered B/BN, and implanted BN films deposited on Ni-coated Si wafers.

Fig. 2 Hardness (GPa) variation with the indenter depth (nm) for the nanoindentation measurement of the B, BN, layered B/BN, and implanted BN films deposited on Ni-coated Si wafers.

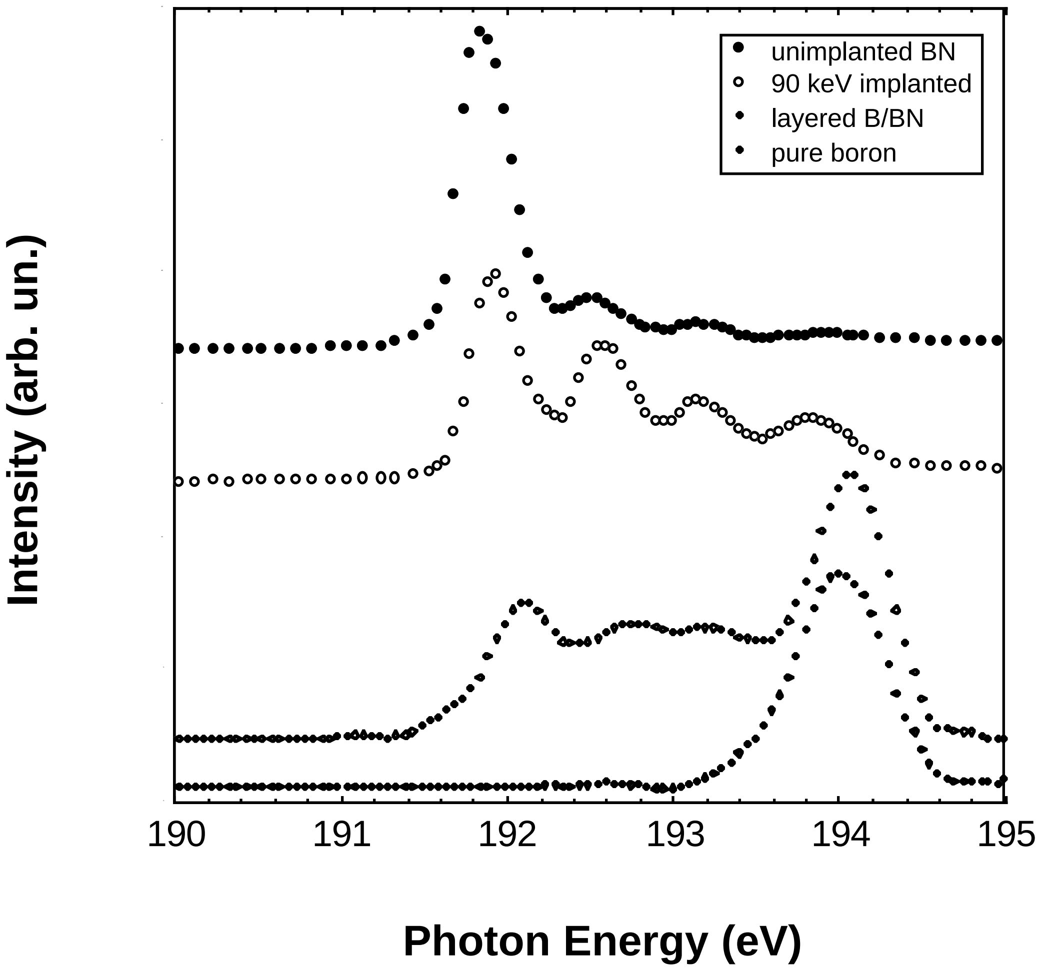
unimplanted BN
90 keV implanted
layered B/BN
pure boron
Intensity (arb. un.)
Photon Energy (eV)
190
191
192
193
194
195

Figure 1.

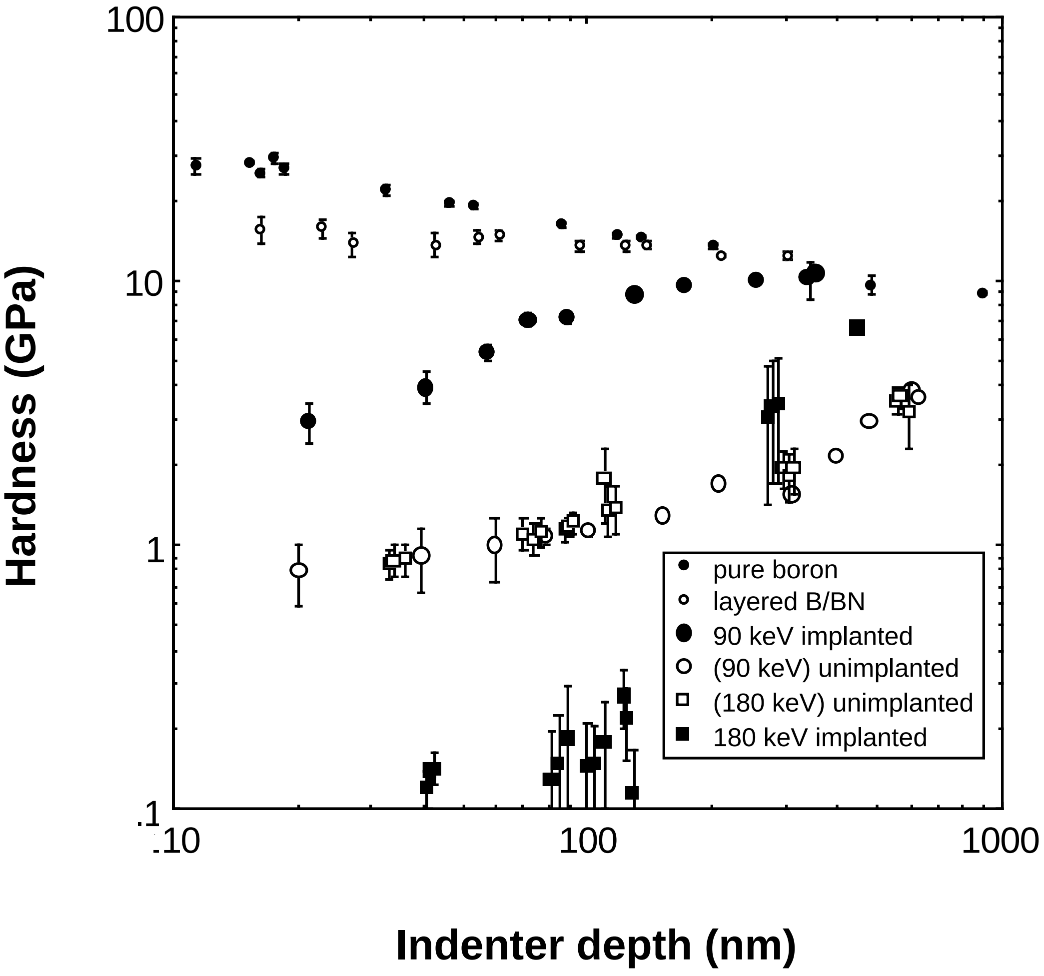
100
10
1
.1
.10
100
1000
Hardness (GPa)
Indenter depth (nm)
pure boron
layered B/BN
90 keV implanted
(90 keV) unimplanted
(180 keV) unimplanted
180 keV implanted

Figure 2.