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NEAR-EDGE X-RAY ABSORPTION FINE STRUCTURE EXAMINATION OF CHEMICAL BONDING IN SPUTTER DEPOSITED BORON AND BORON-NITRIDE FILMS

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ABSTRACT

Near-edge x-ray absorption fine structure (NEXAFS) is used to examine the chemical bonding in boron and boron-nitride films sputter deposited from a fully-dense, pure boron target. Reactive sputtering is used to prepare the boron-nitride and multilayered films. Although the process of sputter deposition often produces films that lack long range order, NEXAFS reveals the distinguishing features of sp^2 and sp^3 hybridization that are associated with different crystalline structures. The sensitivity of NEXAFS to local order further provides details in bonding modifications that exist in these 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]

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.[6-8] The working gas composition, substrate temperature and bias are deposition parameters known to effect the formation of different BN phases.[9] The sputter deposition of boron and boron nitride multilayer films will be pursued to produce stress-free films that are both hard and wear resistant. The multilayer will consist of a hard B layer alternating with a compliant BN layer. The compliant layer may moderate any residual stresses that are formed within the hard layer.

EXPERIMENTAL

The synthesis of the elemental boron film proceeds from the rf sputter deposition of a pure boron target using an unbalanced planar magnetron.[7-8] The deposition system is cryogenically pumped from atmospheric pressure to a base pressure of 5.3×10^{-6} Pa in 12 hrs including a 4 hr, 100 °C bake out. Several reports indicate that epitaxial growth of cBN can be enhanced through the use of nickel epilayers.[10] As such, 20-50nm of nickel are initially sputter deposited onto the silicon wafer substrates for the BN depositions.[9] The substrate table is positioned 9 cm horizontally away from the center of the 6.4cm diameter boron target. The substrate temperature 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^{-1}. A partial flow of N_2 is incorporated to yield a 0 to 55% range of gas composition. The deposition rate is monitored with a calibrated 6 MHz Au coated quartz crystal. An increase in applied forward power from 100 to 300 W produces a linear increase in deposition rate from to 0.007 to 0.021 nm s^{-1}. The deposition of the multilayer structures proceeds by cycling the gas composition between Ar and Ar-25%N_2. A 200 W forward power is used to produce a 0.15-0.16 μm total

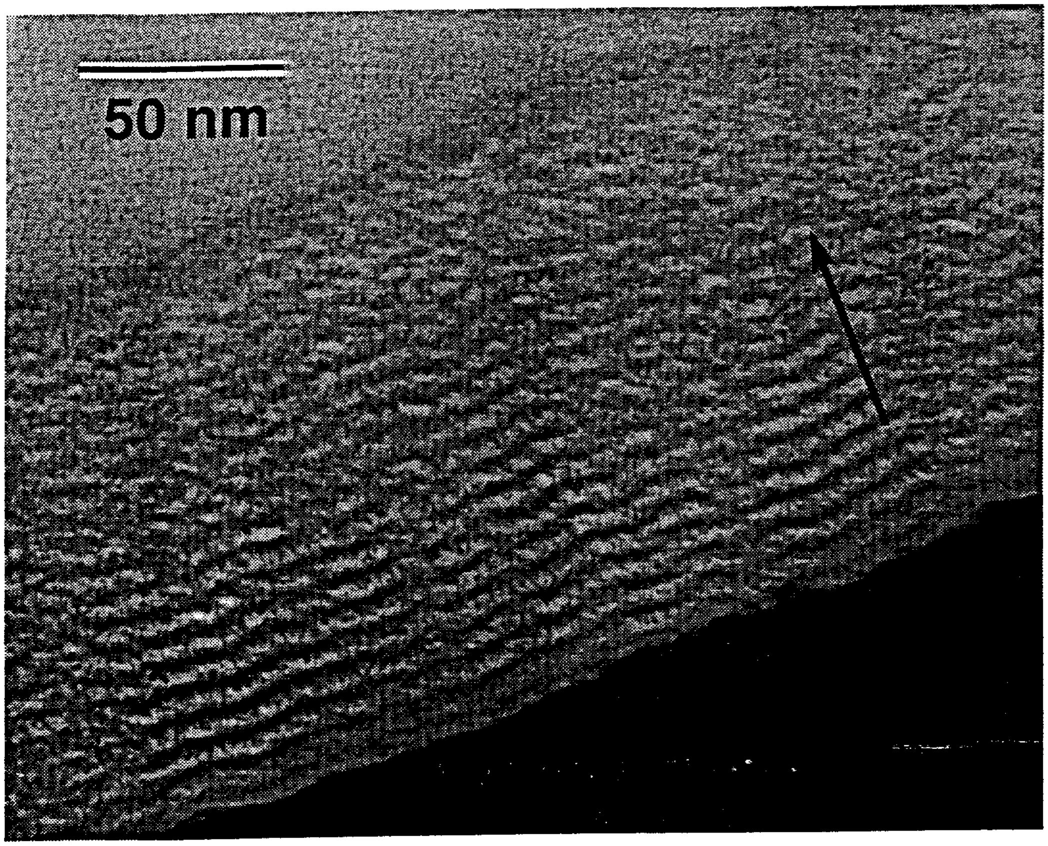

Figure 1. A bright field image of the 20 layer pair B/BN film reveals a 7.5nm repeat spacing along the growth (arrow) direction.

film thickness. The low deposition rate of 0.014 nm s^{-1} combined with the 15-20 sec time interval needed to stabilize the flow rate yields a nominal interfacial width less than 0.3 nm. A nominal multilayer spacing of 7.5 nm is made on the nickel-coated silicon wafers (heated to 225 °C) corresponding to 20 layer pairs.

RESULTS

The boron nitride thin films are characterized for composition, morphology, and chemical bonding. The BN films have a N:B composition ratio of 4:5 as measured using Auger electron spectroscopy (AES) coupled with depth profiling.[9] Transmission electron microscopy (TEM) is used for the assessment of the multilayer film morphology. The B/BN sample is prepared for imaging in cross-section. A bright field image of the B/BN film near the defocus condition reveals the layered structure (Fig. 1). The 20 layer pair structure has a measured repeat spacing of 7.5nm along the growth direction (indicated by the arrow). The layers are continuous, of equal thickness, and conformal to the substrate surface. This is no clear indication of a columnar grain structure so often associated with sputter deposited thin films. Minimal crystallographic information is obtained using TEM for the B, BN and B/BN films. Selected area diffraction of B film indicates it is amorphous whereas both the BN and B/BN multilayer films have diffuse ring patterns with interplanar spacings that most closely fit a disordered hBN phase.[9]

A method to further characterize the films is needed which will provide information as to the chemical bonding within the films and multilayer as well as the interfacial effects between layers. Near-edge x-ray absorption fine structure (NEXAFS) associates unique spectral features in the boron and nitrogen 1*s* photoabsorption cross sections with resonances that are specific with the discrete phases of BN.[11] The photon energy of monochromatic synchrotron radiation is scanned through the core-level edge while monitoring the electron yield to measure

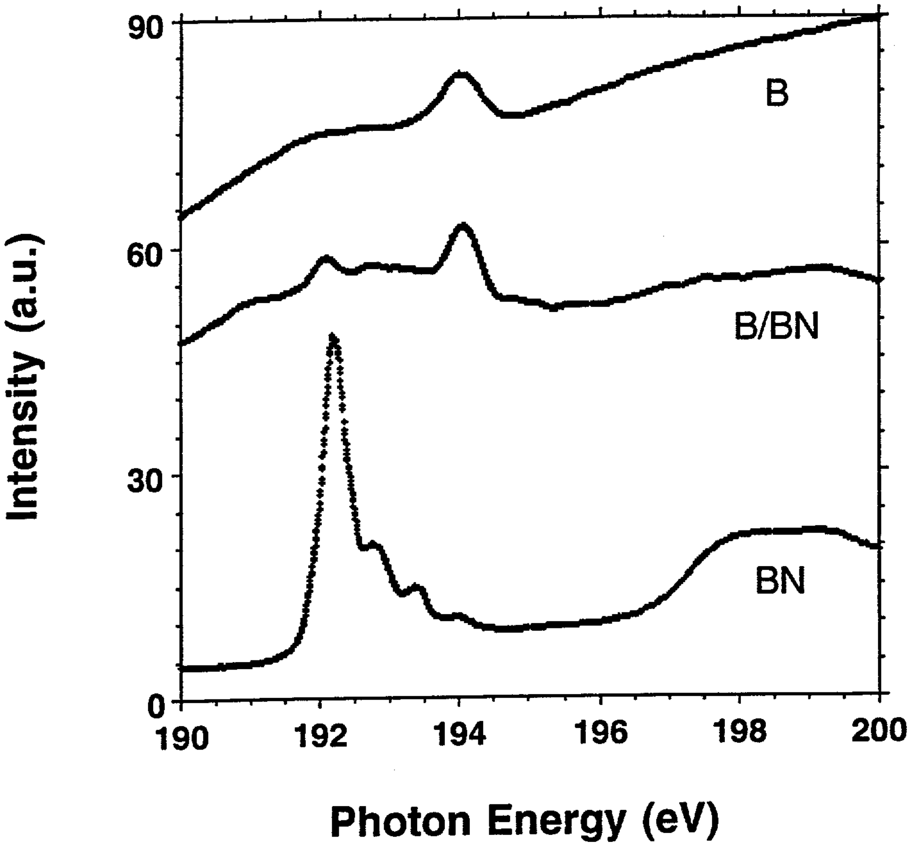

Figure 2. Near-edge x-ray absorption fine structure of the B, BN and B/BN films associates unique spectral features in the B 1*s* photoabsorption cross section with resonances that are specific with the discrete phases of BN.

the core-level photoabsorption cross section. The low-energy, long mean-free-path electron emission dominates the signal yielding a bulk sensitive measurement of the films. Examples of distinguishing features in the NEXAFS spectrum for B and BN films are noted as follows.[11] The sp^2 hybridized, planar bonding that is characteristic of hexagonal BN appears as a narrow and intense transition at 192.0 eV. This π^* resonance is absent in sp^3 tetrahedrally bonded materials as cubic BN which uniquely evidence an absorption maximum step into σ^* continuum states at 194.0 eV. The presence of nitrogen void defects in hexagonal BN has recently been found to be indicated by three satellite peaks above the 192 eV peak in the B 1*s* spectra.[12] Noting that the 192 eV peak is indicative of B-(N_3) bonding in hexagonal BN, the additional peaks correspond in progression with B-(BN_2), B-(B_2N) and elemental boron. These features are evident for the BN film (Fig. 2). A *diffuse peak* for the elemental B film at 194 eV (Fig. 2) can be interpreted as correlating with some degree of planarization of an sp^3 tetrahedral bonding similar in signature to a B sub-surface layer that can be formed in silicon.[13]. The B/BN multilayer contains spectral features (Fig. 2) that comprise the constituent B and BN layers.

SUMMARY

Magnetron sputter deposition is used to prepare B, BN and adherent B/BN multilayer films from a dense, elemental B target. TEM is used to characterize film morphology but does not prove sufficient to detail the crystallinity of these films. Details of the chemical bonding found using NEXAFS for the B and BN films are found superimposed in the B/BN multilayer. NEXAFS characterization will be invaluable to interpret the mechanical behavior of the B, BN and B/BN films in an ongoing nanoindentation examination of hardness.

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