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Deposition of B_4C/BCN/c-BN multilayered thin films by r.f. magnetron sputtering

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Abstract

Thin films of cubic boron nitride (c-BN) and B_4C/BCN/c-BN multilayers, were deposited by r.f. (13.56 MHz) multi-target magnetron sputtering from high-purity (99.99%) h-BN and a (99.5%) B_4C targets, in an Ar (90%)/N_2 (10%) gas mixture. Films were deposited onto silicon substrates with (100) orientations at 300 °C, with r.f. power density near 7 W/cm^2. In order to obtain the highest fraction of the c-BN phase, an r.f. substrate bias voltage between − 100 and − 300 V was applied during the initial nucleation process and − 50 to − 100 V during the film growth. Additionally, B_4C and BCN films were deposited and analyzed individually. For their deposition, we varied the bias voltage of the B_4C films between − 50 and − 250 V, and for the BCN coatings, the nitrogen gas flow from 3% to 12%. A 300-nm-thick TiN buffer layer was first deposited to improve the adhesion of all samples. X-ray diffraction patterns revealed the presence of c-BN (111) and h-BN phases. FTIR spectroscopy measurements indicate the presence of a peak at 780 cm^{-1} referred to as "out-of-plane" h-BN vibration mode; another peak at 1100 cm^{-1} corresponds to the c-BN TO mode and the "in-plane" vibration mode of the h-BN at 1400 cm^{-1}. BN films deposited at 300 °C at a pressure of 4.0 Pa and under − 150 V of nucleation r.f. bias, applied for 35 min, presented the highest c-BN fraction, near 85%. By using 32 layers, it was possible to deposit a 4.6-μm-thick c-BN film with adequate mechanical properties and good adhesion to the substrate.
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Keywords: Cubic boron nitride; Magnetron sputtering; Multilayers; Hard coatings adhesion improvement

1. Introduction

The hexagonal phase of boron nitride (h-BN) has a layered sp^2-bonded structure similar to graphite [1], while the cubic phase (c-BN) is a hard sp^3-bonded diamond-like phase with a cubic zinc blende structure. Cubic boron nitride has a number of extreme and highly desirable mechanical, thermal, electrical, and optical properties. c-BN has a Vickers hardness close to 4500 kg/mm^2, ranking it second in hardness, after diamond, hence, a natural candidate for hard, protective coatings. The fact that c-BN does not react with ferrous metals (as does diamond) makes it even more attractive compared to diamonds for tooling applications or as an abrasive material [2]. c-BN thin film deposition is typically accomplished using ion-assisted methods that generate energetic species of tens to hundreds of electron volts, facilitating the nucleation of the c-BN phase, simultaneously inducing significant compressive stress, which leads to film delaminating, limiting the achievable thickness of the films to approximately 100 nm and creating difficulties for their technical applications [3]. Numerous works have been focused on reducing residual stress and/or improving film adhesion [4,5]. The aim of this work was to improve the adhesion of c-BN films via a multi-step process on (100)-oriented silicon substrates coated with a B_4C layer and a subsequent B−C−N gradient layer as well as multilayers of these two components. Herein, we report the results of B_4C/BCN/c-BN multilayered thin films deposited on Si.

2. Experimental

A boron carbide−boron carbonitride−boron nitride thin-film system was deposited via a multi-target r.f. magnetron sputtering at a frequency of 13.56 MHz and by the application

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of an r.f. bias. The deposition system consists of two cylindrical 4-in. magnetron cathodes (Torus 4HV) powered by two RFX600 generators through two ATX600 matching units. Sputtering was performed with 550 W of RF power applied to the targets. The targets consisted of a single-phase 4-in.-diameter and 0.16-in.-thick h-BN disk with purity above 99.9% and a B_4C (99.5% purity) target with similar dimensions, mounted on a water-cooled Cu holder. The deposition chamber was initially pumped down to less than 5×10^{-4} Pa, using a turbomolecular pump and then a mixture of purified Ar and N gas, or only pure Ar gas was introduced into the chamber. During the growth, chamber pressure was maintained at 6.7×10^{-1} Pa. The target was 50 mm from the substrate holder. 0.3-mm-thick silicon wafers with (100) orientation covered with a 300-nm-thick TiN buffer layer were used as substrates. Targets and substrates were sequentially pre-sputtered at 80 W at a pressure of 2.7 Pa in an Ar atmosphere for 20 min. B_4C was first deposited in a pure Ar atmosphere. Subsequently, a BCN gradient layer was sputtered by introducing additional N_2 gas into the chamber. Finally, we carried out the BN deposition by using the h-BN target and a mixture of Ar and N_2 gases. The growth rate for B_4C, BCN, and BN was approximately 0.3 nm/s, 0.1 nm/s, and 0.4 nm/s, respectively, for bias voltages between -40 V and -150 V. Films were characterized by X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS), and energy-dispersive X-ray spectroscopy (EDX). Tribological properties like hardness, elastic Young's modulus, and adhesion were determined by nanoindentation measurements.

3. Results and discussion

For the purpose of investigating the dependence of BN phase evolution with the bias voltage, BN films were prepared at different r.f. bias voltages between -50 V and 350 V. The existence of a substrate bias threshold for c-BN formation (-90 V) can be understood by considering how BN transforms from a thermodynamically stable h-BN structure to a higher energy c-BN structure. This transformation requires a hybridization change from sp^2 to sp^3 accompanied by a reduction of the inter-planar spacing, which cannot be accomplished without both bonds breaking, thus changing the chemical nature of the bonds [6].

The BN film, deposited at a substrate temperature of 300 °C in an atmosphere of 4×10^{-2} mbar and with a bias voltage of -150 V r.f, presented the highest c-BN fraction–85%–as determined by FTIR analysis under the assumption that the in-plane h-BN peak at 1400 cm^{-1} and the c-BN TO peak at 1100 cm^{-1} both have similar absorption coefficients. The c-BN fraction increased to -150 V and then decreased due to the re-sputtering phenomena. Once we got the proper conditions to obtain c-BN films, we deposited single boron carbide coatings and boron carbonitride films, as well as multilayers of both materials with an overlayer of c-BN onto silicon substrates The selected sample group was labeled B_4C-1, B_4C-2, B_4C-3, BCN-1, BCN-2, BCN-3, Multilayer-1, Multilayer-3, Multilayer-5, and Multilayer-16, respectively.

Through XRD analysis of the three deposited specimens of boron carbide films, we found only the peak of graphite at $2\theta=26.7°$ and silicon at $2\theta=69.1°$. This is the typical case for amorphous films with a carbon content greater than 20% [7]. Polycrystalline boron carbide films are only possible if deposition temperature is greater than 900 °C. These observations agree with other works [8,9].

Surface morphology was analysed using a high-resolution scanning electron microscope (Philips XL 30 FEG) equipped with a light element-sensitive EDAX EDX system with a resolution of 1 nm at 30 kV and an atomic-force microscope (Thermo microscopes CP Research) geared with a 100-μm scanner, in-contact mode with 22 nN, and a cantilever CSC 21/TO Antatec.

Fig. 1a shows two 5×5- and 2×2-μm^2 AFM micrographs for samples B_4C and BCN-3. Both samples seem homogeneous and dense and the micrographs reveal granular and homogeneous surfaces with grain size between 125 nm and 200 nm with surface roughness of 2.7 nm and 0.9 nm for B_4C-2 and BCN-3, respectively. The cross-sectional SEM images showed a first columnar 300-nm-thick TiN adhesion layer followed by dense and amorphous 700-nm- and 1100-nm-thick boron carbide and boron carbon nitride films, respectively, as displayed in Fig. 1b. This observation indicates a columnar growth of the film according to observations made by Lee [8], Chiang [9], and Eckardt [10]. The same behavior was also observed in B_4C-1, B_4C-3, BCN-1, and BCN-2 samples.

With AFM measurements, it was possible to determine grain size and roughness of the BC and BCN samples and their dependence on the bias voltage. Both parameters increase with the bias voltage due to the increasing ion bombardment of the sample surface. Similar results were obtained by Cao et al. [11]. Vickers hardness measurements of the boron carbide and boron carbon nitride films, along with hardness and fracture toughness of the deposited multilayer system coatings was performed by using a microindenter (LECO M-400-G2 at 2000× optical magnification). This indenter was a four-corner diamond pyramid with an approach angle of 136°. The following relationship was used to determine hardness and fracture resistance [9,12]:

$$HV = 0.1891*\frac{F}{d^2} \tag{1}$$

$$Kc = 0.092*\sqrt{\frac{HV*F}{(0.25*l + 0.5*d)}} \tag{2}$$

HV=Vickers hardness in N/m^2, F=load in newtons, L=crack length in meters, and d=diagonal length of Vickers print in meters. The factor 0.092 involves the influence of the indenter material and geometry. We used 50- and 100-lb loads. This method causes errors near 15%. Due to intense ion bombardment of the film surfaces, both film density and hardness increased. The BCN thin films contain additional formations of the cubic BN phase, contributing to an increase in the hardness, in accordance with Eckerdt [10] and Cao [11].

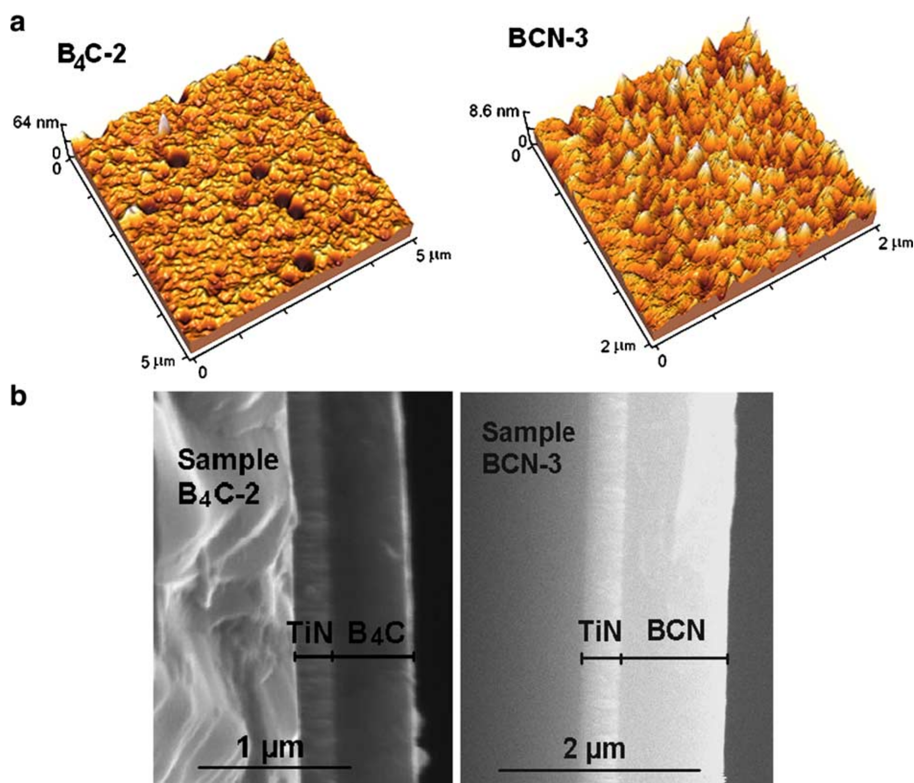

Fig. 1. (a) AFM surface image (5 × 5 µm) for B_4C and (2×2 µm) for BCN single layers deposited on (100) silicon substrates at 300 °C. (b) SEM cross-sectional view of B_4C and BCN single layers deposited on (100) silicon substrates at 300 °C.

To determine the chemical composition and bonding states of the films, X-ray photoelectron spectroscopy (XPS) was performed using a surface characterization UHV system featuring a Specs PHOIBOS 100 hemispherical analyzer and a Specs XR-50 twin anode operating at 100 W. Excitation energy of Al $K\alpha_{1,2}$ E = 1486.65 eV was used. As a second verification, energy dispersive X-ray spectroscopy (EDX) was performed. The stoichiometry at various deposition bias voltages and gas flows was calculated by the ratios of B1s, C1s, and N1s peaks, appearing in BC and BCN films. The strongest bonding states of the photoemission lines B1s (188.4 eV and 190.8 eV9), C1s (283.6 eV and 286.1 eV), and N1s (398.4 eV and 398.9 eV) indicate that the films are mostly composed of BC, BCN phases with additional small contents of CN phases [13]. Also, the existence of free boron (B–B), free carbon (C–C), oxygen, and argon is evident as a contaminant source coming from the targets and work atmosphere. Individual peak analyses, as shown in Fig. 2a–f, reveal the aforementioned. Through XPS analysis, we found the following chemical compositions for BC and BCN phases deposited at −40, −60, and −100 bias V, respectively: $B_{4,5}C$; $B_{4,2}C$; $B_{3,5}C$; $B_{0.47}C_{0.43}N_{0.37}$; $B_{0.46}C_{0.35}N_{0.36}$, and $B_{0.45}C_{0.41}N_{0.42}$. Based on the above results and on the samples, which combined good mechanical properties and the best stoichiometry, we selected the process parameters for samples B_4C-2 and BCN-3 to deposit the multilayer system. For the deposition of the BCN thin layer, a step-by-step nitrogen gas flow of 3%, 6%, and 12% was added to the Ar/N mixture to obtain the gradient layer of BCN. For our multilayered thin films, we selected a number of 2, 6, 10, and 32 layers. Each bilayer was composed of a 170-nm-thick B_4C monolayer and a 70-nm-thick BCN gradient layer.

A SIMS Cameca IMS 5F with a 12.4-kV O^{+2} ion beam and an arc current of 5.6 mA was used to determine the chemical-depth distribution of the elements boron, carbon, and nitrogen in the multilayer of sample B_4C/BCN/c-BN-1 with 2 layers, shown in Fig. 3. The existence of only high signals of boron and nitrogen at the surface for the first 500 s sputter time, corresponding to the c-BN film is evident. At this thickness, nitrogen signal goes down slowly, while the carbon signal increases. This is actually the expected behavior for the BCN gradient layer. For a 1400- up to 2400-s sputter time, the carbon signal is very high and the nitrogen signal weakens, indicating the formation of the boron carbide phase. As of this sputter time, the titanium signal and again the nitrogen signal appear corresponding to the TiN buffer layer. Maintaining deposition parameters of the above sample (B_4C/BCN/c-BN-1), we deposited multilayers with 3, 5, and 16 B_4C/BCN bilayers. Fig. 4 shows the SEM cross-sectional image of deposited multilayers. In the case of a 16 bilayer sample (B_4C/BCN/c-BN-4), it was possible to deposit a 4.6-µm-thick cubic boron nitride film free from delamination.

Hardness and fracture toughness increased together with the number of bilayers from 42 to 54 GPa and from 3.7 to 5.1 MPa $m^{1/2}$, respectively, as shown in Fig. 5.

This behavior may have a twofold explanation; first, the inclusion of the boron carbide films present better adhesion to silicon than BN. Second, the application of a softer layer and

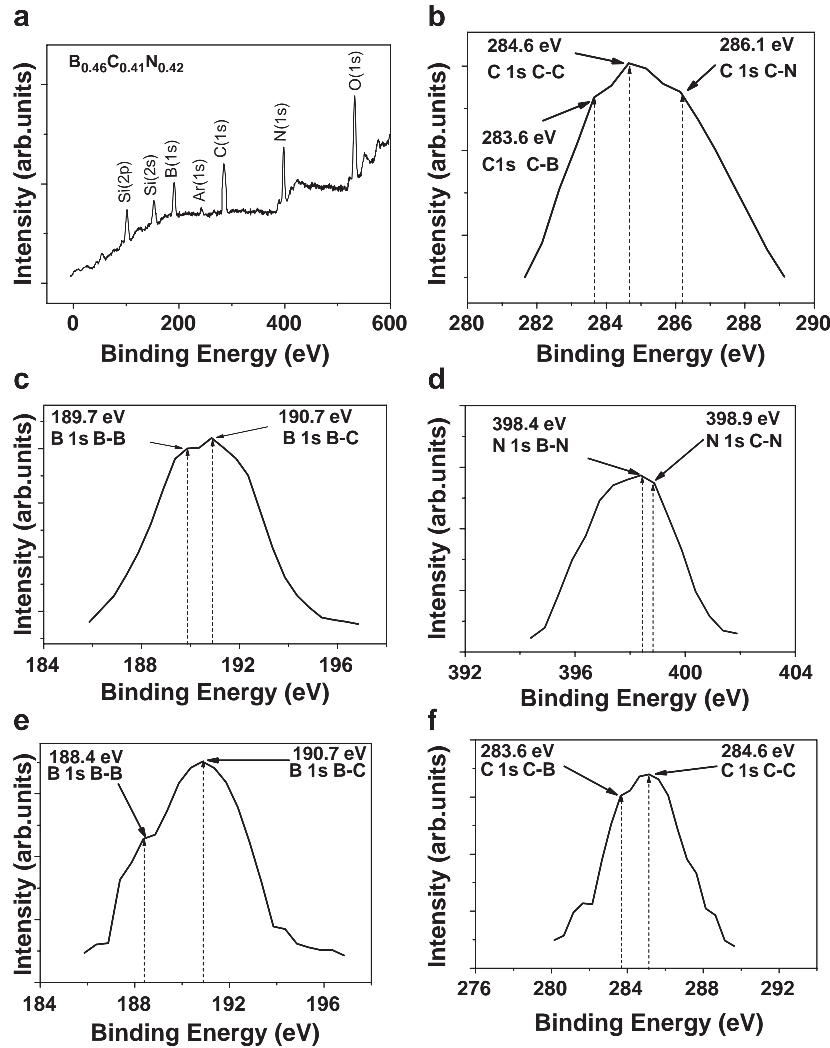

Fig. 2. (a) complete XPS spectra for a $B_{0.46}C_{0.41}N_{0.42}$, single layer deposited under a bias of − 100 V. (b–d) correspond to their B1s, C1s, and N1s XPS peaks (e and f) correspond to a single layer of B_4C, as indicated.

sp^2-bond richer BCN films allowed a smooth transition of important mechanical properties like hardness and fracture toughness from substrate to the c-BN surface. The formation of a textured h-BN (t-BN) before the nucleation of c-BN causes the film to delaminate for thicknesses above 150 nm,

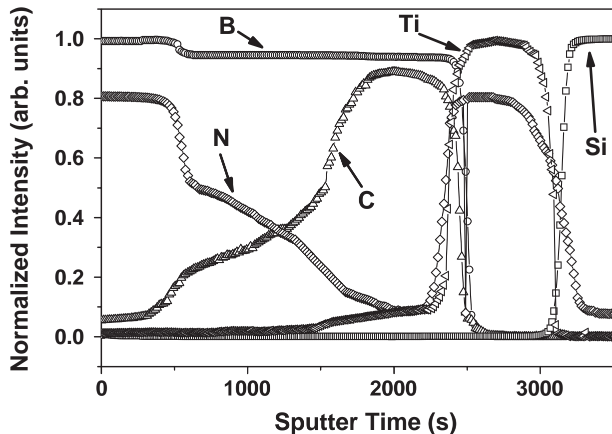

Fig. 3. SIMS depth profile of a B_4C/BCN/c-BN bilayer on (100) Si substrate.

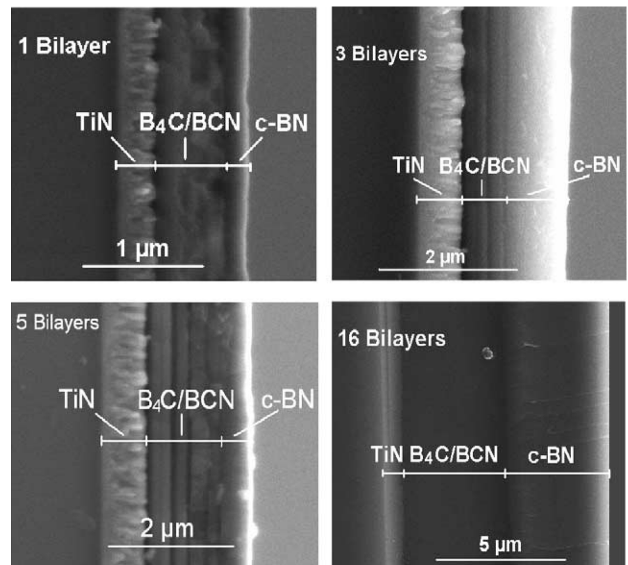

Fig. 4. SEM cross-sectional view of a B_4C/BCN/c-BN on (100) Si, containing 1, 3, 5, and 16 bilayers, respectively.

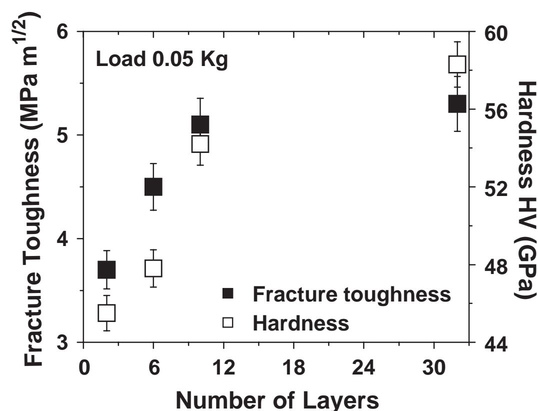

Fig. 5. Dependence of hardness and fracture toughness in multilayers as function of the number of layers.

due to the low shear resistance of t-BN at the interface with the substrate. The introduction of the TiN adhesion as well as the B_4C layers contributes to the increase in the shear resistance of the multilayer and thereby their adhesion to the substrate [5].

Furthermore, the nanometric grain size of the boron carbide and boron carbon nitride phases and the number of the interfaces in the multilayers become an obstacle for moving micro-cracks and dislocation, leading to an increment of hardness, fracture toughness, and E-module of the coating system [4,5,14].

4. Conclusions

Through the use of a B–C multilayer and a B–C–N gradient, the deposition of thick and stable c-BN coatings of up to approximately 4642 nm on silicon substrates was possible. The appropriate structural and mechanical properties of both coating types played the most important role for hardness increase, as well as an improvement in toughness and adhesion of the cubic boron nitride. The hardness of c-BN as well as the structural and mechanical properties of B_4C and BCN thin films agreed well with previously reported works for these materials. A substantial improvement in the mechanical properties and adhesion was obtained by producing multilayers based on these compounds.

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