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Boron carbide coatings prepared by cathodic arc deposition

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Boron carbide films are attractive materials for use as tribologcal coatings for low and high operating temperatures, especially for applications that require high hardness. The properties of boron carbide films prepared by cathodic arc using a heated B_4C cathode are investigated. The B:C ratio in the film was about 3, and the only detected impurity was oxygen with a content below 5%. The effect of substrate bias on the film characteristics was studied. A direct correlation between hardness and elastic modulus and bias voltage applied to the substrate was observed for bias voltages in the interval of 0–500 V. Microstructure and chemistry of the films were investigated using X-ray diffraction, electron microscopy and X-ray absorption spectroscopy. © *2003 Kluwer Academic Publishers*

1. Introduction

B_4C is an attractive hard coating for a variety of applications. Interestingly, it has the highest hot-hardness of the known materials, i.e., hardness at temperatures around 800°C. Moreover, B_4C has very high lubricity, and thermal and chemical stability.

There is a strong dependence of the properties of B_4C on its microstructure, and therefore on the processing conditions. Chemistry and structure play a fundamental role in defining the functional properties of B_4C. According to the equilibrium B—C phase diagram [1], up to 1000°C the "B_4C" phase has a large solubility interval. It can have any composition in the interval $B_{91}C_9$ to $B_{78}C_{22}$. The crystal structure of B_4C is complex, particularly the non-stoichiometric phases (i.e., $B_{4-\delta}C$). First-principle calculations combined with infrared absorption and Raman data suggest that the atomic structure of B_4C consists of one $B_{11}C$ icosahedron with carbon atoms at a polar site, and a chain of C—B—C [2, 3]. As the C content decreases, the C—B—C chains are replaced by C—B—B chains[3]. The structure of amorphous B_4C is viewed as a network of randomly distributed icosahedra.

B_4C films have been prepared by several plasma based techniques [4–8]. In this article some results on the synthesis of B_4C using Metal Plasma Immersion Ion Implantation and Deposition are presented. This technique makes use of a cathodic arc plasma source, and the application of a bias to the substrate. Cathodic arc deposition has been shown to be a very attractive method for the formation of hard coatings [9, 10]. The major difficulty in preparing B-based coatings using arcs is the poor electrical conductivity of B or B-compounds of interest at room temperature. Of interest here, the electrical resistivity of B_4C at room temperature is 10 $\Omega \cdot$cm, and in order to be best used as a cathode, it requires external heating (at 500°C the resistivity approaches 0.4 $\Omega \cdot$cm). The brittleness of B_4C is yet another difficulty in the use of this material as a cathode, for it has low resistance to thermal shock.

2. Experimental details

Most of the films used in this investigation were prepared using pulsed vacuum arc plasma sources designed and built at HY-Tech Research Corporation (Radford, VA). The cathode consisted of sintered B_4C rods with approximately 25 mm in diameter. The cathode was heated to 600°C in order to decrease the electrical resistivity and to improve its mechanical stability during the arc pulses. The source has been described in detail elsewhere [11]. For purposes of comparison, some boron-carbon films were also prepared with another plasma source, designed at Lawrence Berkeley National Laboratory (LBNL), which used a 6 mm diameter rod as the cathode without any external heating [12]. Films produced by the LBNL source were all C-rich and will not be discussed in great detail in this article.

The depositions were carried out at substrate temperatures of 25°C and 600°C. In order to evaluate the effect of ion energy during deposition on the film structure, the depositions performed at room temperature

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were carried out with and without a substrate pulsed bias voltage of −100 V and −500 V. The duration of the arc pulses was 250 ms (for the HY-Tech source). The deposition was carried out in the low 10^{-4} Pa pressure. Most of the depositions were performed on highly doped (100) silicon wafers, and a few depositions were performed on mirror polished steel.

Elemental composition of the films was determined by Rutherford Backscattering Spectroscopy (RBS) using a 2 MeV He^+ beam. Near edge X-ray absorption fine structure spectroscopy (NEXAFS) was used to analyze the bond chemistry of these films. NEXAFS spectra were taken using synchrotron radiation at the beamline 7.3.1.1 at the Advanced Light Source. This is a bending magnet beamline that covers the 175–1500 eV spectral range, which contains the K-edges of the light elements (B, C, O, N and F), the L-edges of the 3d transition metals and the $M_{4\text{-}5}$-edges of the rare-earths [14]. Graphite and a diamond crystal were used as sample references for the energy calibration. The NEXAFS spectra were taken in a total electron yield mode by measuring the current from the sample to ground.

The microstructure was determined by X-ray diffraction with a SIEMENS D-5000 diffractometer and by transmission electron microscopy (TEM) with a Phillips CM200 (0.23 nm point resolution) with PEELS (Parallel Electron Energy Loss Spectrometer). Nanoindentation was performed by using the Hysitron Picoindenter coupled with an atomic force microscope. The area function of the cube corner diamond tip was obtained by calibration against an Al_2O_3 (0001) single crystal and quartz. Penetration depth was kept at less than 10% of the film thickness and the values presented correspond to averages of five individual indentation measurements.

3. Results and discussions

The films prepared with the HY-Tech source have B and C as the primary constituents, as determined by PEELS and Rutherford Backscattering Spectroscopy. The concentration of other elements in the film did not exceed 5 at%. The B:C ratio in the films prepared using the hot-cathode varied from 2.5 to 3.3. In a recent work Kokai *et al.* [13] have shown that Pulsed Laser Deposition from sintered B_4C target produced films with B:C ratio varying from 1.8 to 3.2, with the highest ratio obtained at the highest fluence. A likely reason for the lower B:C ratio in the films is the precise composition of the cathode material. Although the cathode was made from pure B_4C powder, the presence of sintering agents has resulted in a cathode with composition slightly off-stoichiometric. Other reasons that may influence the final composition of the films are: (a) the angular distribution of the ion flux depends on the chemical element itself; (b) differences in sputtering rates of B and C in the film. X-ray diffraction of the cathode in fact demonstrated that in addition to B_4C, some C-phases could be found as well.

The surface topography of the film prepared without filtering is rough, primarily because of macroparticles. A typical AFM image of a film deposited without filtering is shown in Fig. 1. On the contrary, but not shown here, films prepared with macroparticle filtering were much smoother.

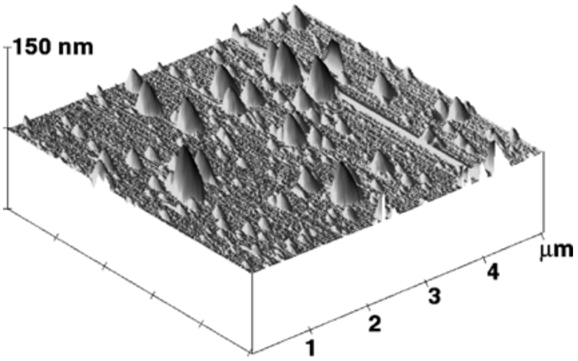
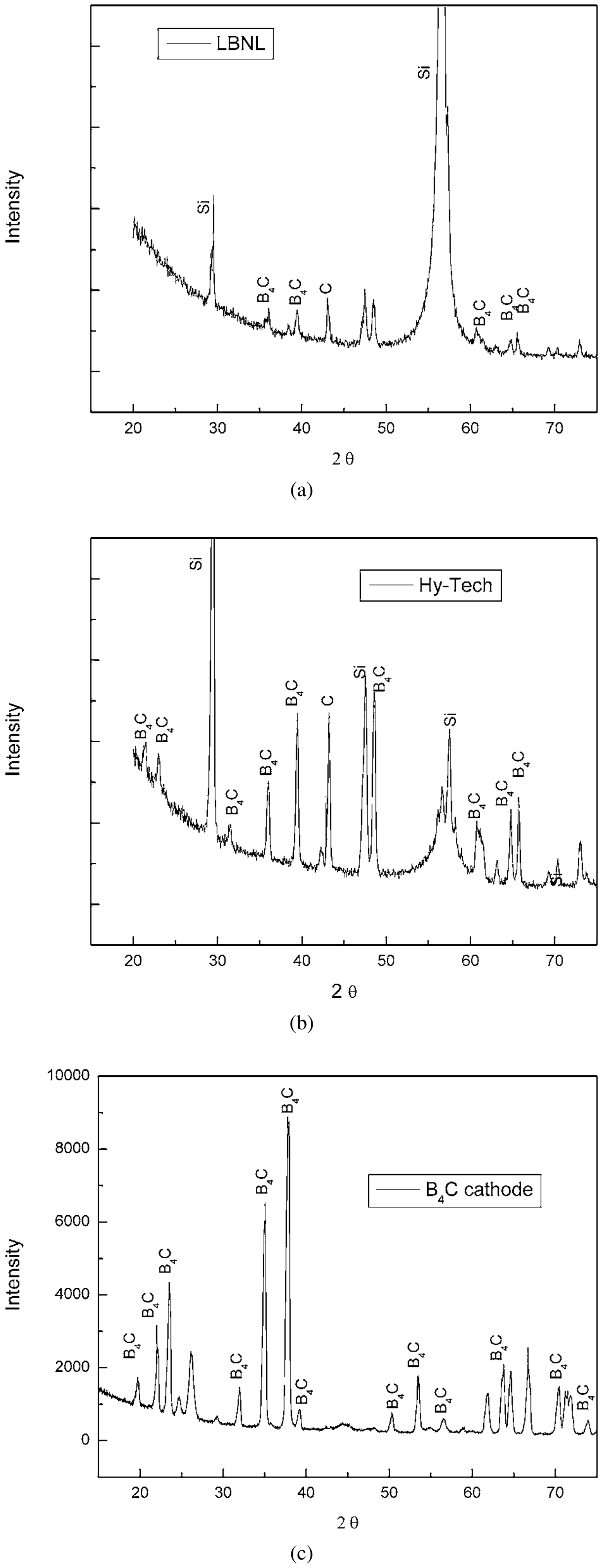


Figure 1 Atomic Force Microscopy of a 350 nm thick boron carbide film prepared using the unfiltered plasma source with the heated cathode. The substrate temperature during deposition was 600°C.

The diffraction pattern obtained by glancing angle X-rays at 4° incidence indicates that crystalline B_4C was present in the film. In an attempt to determine whether the origin of the crystalline phase was the incorporation of macroparticles or not, X-ray diffraction patterns from films deposited with and without a macroparticle filter were obtained. Since the HY-Tech source did not have filtering capabilities at the time this investigation was performed, the LBNL source was used. Filtering prevents macroparticles from arriving at the substrate because the substrate is not in direct line of sight with the cathode. As shown in Fig. 2a, crystalline B_4C was also found in the film prepared with filter. Therefore at least in part some of the crystalline B_4C is formed from the deposition of the ionic species. In an earlier work [11], it was concluded, from electron diffraction and normal incidence X-ray diffraction of similar films, that the films were predominantly amorphous. On the other hand, the present results, with glancing angle, indicate the presence of crystalline phases. The discrepancy between these two results may be attributed at least partially to the small scattering cross section of B and C, the small probed film volume with normal incidence X-ray, and the small probed volume in TEM.

The diffraction patterns shown in Fig. 2a–c have peaks that are attributed to boron carbide and silicon, and in addition show peaks that have been tentatively related to a crystalline carbon phase (JCPDS 26-1081), labeled C. Based on the equilibrium phase diagram of the B—C system [1], films with a B:C ratio below 3.3 should consist of mixtures of graphite and B_4C, with the graphite content increasing with increasing C concentration.

Most B_4C films prepared by magnetron sputter deposition are amorphous. Shinno *et al.*, who used cathodic arc deposition on molybdenum from cathodes consisting of mixed C and B powders [8], claimed to observe crystalline phases. Their films consisted of a mixture of several phases: amorphous carbon, graphite and B_4C in addition to an interface consisting of molybdenum carbide. The films described here, prepared by cathodic arc from a different cathode, contain both amorphous and crystalline phases as well. The bonding structure of the films prepared here was further analyzed NEXAFS.



(a)

(b)

(c)

Figure 2 X-ray diffraction patterns obtained at glancing angle of 4° of a boron carbide film deposited at (a) 200°C with the macroparticle filter, (b) at 600°C without the macroparticle filter, and (c) of the cathode material used to prepare both films.

The spectrum obtained across the B 1s absorption edge (shown in Fig. 3) is characterized by two sharp peaks at 190.6 eV and 192.2 eV and a broad band from 196 to 208 eV. The 1s absorption edge is characterized by the onset of the antibonding π^* state at 190 eV. The peaks at 190.6 and 192.2 can be associated with the B—B and B—C bonds respectively, in accordance with previously

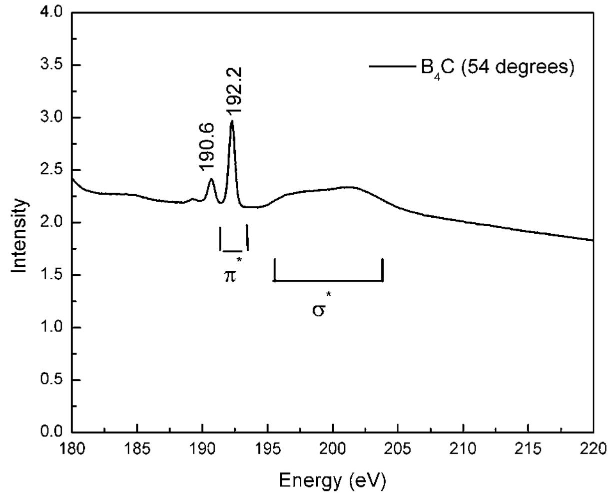


Figure 3 Near-edge X-ray absorption fine structure spectra of the B$_4$C films obtained from a film with composition B$_{3.3}$C across the B 1s absorption edge.

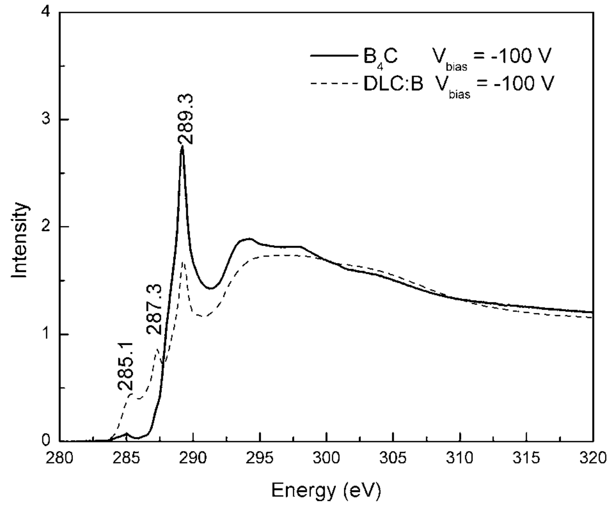


Figure 4 Near-edge X-ray absorption fine structure spectra of the two boron carbide films obtained across the C 1s absorption edge. The dotted curve was obtained from a B-doped DLC film with 5% B, and the solid spectrum was obtained from a film with composition B$_{3.3}$C.

published data [13, 14]. Presence of boron oxide would lead to a peak between 194 and 195 eV, which has not been observed. The band from 196 to 208 is related to the σ^*.

The width of the two peaks in the π^* region at half maximum (FWHM), 0.7 eV, is comparable to that observed in B$_4$C nanowires [15] and narrower than films prepared by PECVD [15] (reported about 1.7 eV). This suggests that the local bonding configuration in these films is similar to that in single crystal B$_4$C, despite the structural disorder. The σ^* band is very broad, namely 11 eV, and featureless which is consistent with an amorphous structure.

The spectrum of the B$_4$C film obtained across the C 1s absorption edge is shown in Fig. 4 for the films prepared using the room-temperature cathode and the heated cathode. In addition to that, the spectrum obtained from a film containing 5% B is also plotted in dashed lines. The antibonding π^* state for C is indicated by the peak at 285.2 eV. The peak at 287.2 can be associated to either oxygen or hydrogen contamination, because it may corresponds to the transition C 1s → π^* in C=O or C 1s → π^* in C–H. Since NEXAFS is extremely surface sensitive, and no pre-cleaning of the surface was performed, this peak may be a result of surface contamination. The spectrum obtained from the $B_{3.3}C$ film however did not show this peak, which suggests that such a peak is due to the bulk of the film. Lastly, and more importantly for the purposes of this work, the peak at 289.3 eV can be linked to the excitonic processes in sp^3 bonded amorphous carbon. The enhancement of the peak at 289.3 eV suggests that increasing the B content in the films leads to an increase in the content of sp^3 bonded C.

Elastic modulus and hardness values were determined by nanoindentation. Both values increased when a bias voltage of −100 V or −500 V was applied. Hardness increased from 15.6 GPa to 25.6 when −100 V was used and remained virtually unchanged (26.0 GPa) when −500 V was applied. Similarly the reduced moduli were 162 GPa , 210 GPa and 210 GPa for bias voltages of 0, −100 and −500 V respectively. The hardness value for the film deposited without bias is significantly lower than the values reported for crystalline B_4C, namely 28–35 GPa, but is similar to other amorphous B_4C films prepared by other techniques. On the other hand, application of a bias voltage did in fact increase the hardness to values approaching the range observed in crystalline B_4C. The increase in hardness observed in the films prepared in this investigation is in the same range as the increase in hardness observed in biasing sputter deposited boron carbide films [4].

4. Conclusions

Boron carbide coatings with stoichiometry approaching B_4C have been prepared by cathodic arc deposition and their chemical and mechanical properties were evaluated. At deposition temperatures up to 600°C, the coatings consisted of mixture of amorphous and crystalline phases, and carbon enrichment in the film led to the formation of a graphite-like phase. The elemental composition of the films produced with the heated cathode was similar to that of the cathode material, thus demonstrating that a single plasma source using a boron carbide cathode can be used to produce stoichiometric B_4C. Film hardness and elastic modulus increase with increasing applied bias voltage to the substrate to values approaching that of crystalline B_4C. Maximum hardness of 26 GPa were observed while the hardness of bulk crystalline B_4C has been reported in the range of 28–35 GPa.

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