

CHARACTERIZATION OF BORON-CONTAINING CARBON THIN FILMS (BC_x)

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INTRODUCTION

Boron is of particular interest in the study of carbon. Applications range from oxidation resistant coatings for carbon/carbon composites [1] to anodes for lithium-ion batteries [2]. As a solid state dopant, boron will substitute in graphite up to approximately 2.3 atomic percent [3]. Recently, boron/carbon thin films have been produced with an increased substitutional boron content through chemical vapor deposition (CVD).

Films containing 25 percent substitutional boron (BC₃) were produced by reacting boron trichloride (BCl₃) with benzene (C₆H₆) at 800°C. Combustion in fluorine and infrared absorption spectroscopy of the gaseous mixture established the relative proportions of carbon to boron at 3:1 while electron micrographs and electron diffraction confirmed the graphitic symmetry and sheet-like characteristics of this material [4].

Way and co-workers produced graphitic films with varying amounts of boron (B_xC_{1-x}; 0 ≤ x ≤ 0.17) by reacting boron trichloride with benzene at low pressures [5]. X-ray diffraction studies showed that the d₀₀₂ spacing decreased as the boron content increased and that at 17 atomic percent boron d₀₀₂ was 3.336 Å, significantly smaller than pure graphite. X-ray absorption verified that the boron 1s edge and carbon 1s edge were qualitatively the same, proving that boron was a substitutional species in the graphitic films.

Recent work by Kouvetakis has centered on a different precursor for the production of boron-containing carbon films [6]. Coatings prepared by sublimation of triphenyl boron ((C₆H₅)₃B) have shown promise as a way of producing a material with approximately 5 atomic percent boron. This approach appears to bypass the initial steps associated with the boron trichloride/benzene reaction since the triphenyl boron molecule already has a boron atom trigonally bonded to three carbon rings.

EXPERIMENTAL

BC_x coatings were produced by reacting boron trichloride with benzene at a temperature of 775°C and 1 atm

pressure. Quartz slides, carbon/carbon composites, highly oriented pyrolytic graphite and carbon fibers (T-300 and P-55-S) were used as substrates for the BC_x films. Deposition times ranged from one hour to seven days with a typical experiment lasting two days. Boron trichloride to benzene ratios from 2:1 (BC₃) to 5:1 were used in an attempt to create coatings with a broad range of substitutional boron. After initial deposition the coatings were annealed in helium at 1200°C for 24 hours to remove residual hydrogen and permit some atomic reordering.

Raman spectroscopy and x-ray diffraction (XRD) helped to determine the graphitic nature and d-spacing of the coatings. Nuclear magnetic resonance (NMR) and x-ray photoelectron spectroscopy (XPS) were enlisted to study the localized environment of the boron and bonding configurations while secondary ion mass spectroscopy (SIMS) allowed for qualitative determination of the material content and film uniformity.

RESULTS AND DISCUSSION

Figure 1 illustrates x-ray diffraction data for three films produced via chemical vapor deposition. Film A was produced by reacting boron trichloride with benzene but without an anneal. Film B was produced by only depositing from benzene and then annealing. Film C was produced by reacting boron trichloride with benzene and then annealing. Other than these differences, all other processing conditions remained the same. It is apparent from Figure 1 that an anneal cycle is necessary in order to produce any crystallinity, which from the peak position appears to be graphitic in nature. No other diffraction peaks were observed.

Additionally, boron appears to induce a low temperature reordering of the carbon layers not present in the film deposited from benzene. The d₀₀₂ spacing for the annealed BC_x film is 3.385 Å.

X-ray photoelectron spectroscopy (XPS) of the BC_x coating showed the carbon 1s peak to be present at 285.0 eV, slightly greater than the binding energy of graphite (284.3 eV). The 1s peak for boron was rather broad and

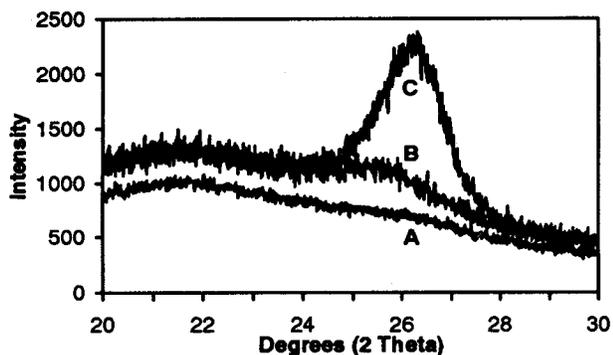


Figure 1: X-ray diffraction patterns for CVD films; (A) BC_x film without anneal, (B) carbon film with anneal and (C) BC_x film with anneal.

asymmetric covering a range of binding energies from approximately 186 to 196 eV with the main peak located at 192.6 eV and minor peaks apparent at 191.0 and 188.2 eV. The presence of numerous peaks for boron is perhaps indicative of the various bonding configurations available to substitutional boron in a disorganized carbon film. These binding energies are significantly higher than those reported for elemental boron (187.1 eV) and B_4C (186.3 eV).

Solid state B^{11} nuclear magnetic resonance (NMR) of the BC_x coating showed a single broad peak. A broad peak suggests that the boron is trigonally coordinated and also bonded to carbon. However, this peak might be overshadowing other narrower boron peaks relating to either tetrahedral coordination or boron to oxygen bonding.

Raman spectroscopy of a carbon film and a BC_x film resulted in peaks situated around those associated with graphitic materials. HOPG has one vibrational mode at 1580 cm^{-1} which is attributed to an in-plane vibration. Additionally, surface structural disorder will cause another vibrational mode at 1355 cm^{-1} . For the carbon film the peaks were located at 1325 cm^{-1} and 1580 cm^{-1} while the peaks for the BC_x coating were at 1335 cm^{-1} and 1570 cm^{-1} . The boron in the BC_x coating has resulted in a shift of the in-plane vibration contrary to what is expected of boron doped graphite [7]. This could be explained by the difference in interlayer spacing between a boron doped graphite and the BC_x coating. Boron doped graphite is expected to have a d_{002} less than that of graphite which would then cause a shift in the graphitic peak to a higher frequency vibration. However, since the d_{002} for BC_x is greater than that of graphite, a shift to a lower frequency vibrational mode would be expected.

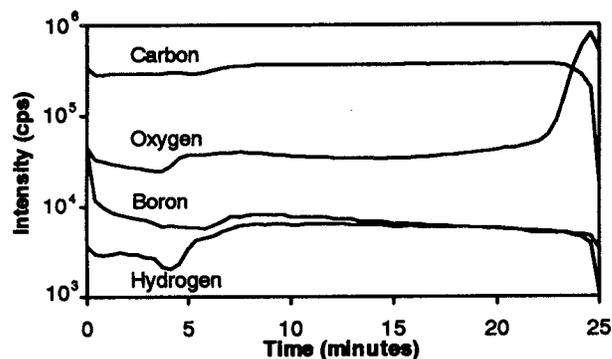


Figure 2: Secondary ion mass spectroscopy depth profile of BC_x film.

Figure 2 shows a secondary ion mass spectroscopy (SIMS) depth profile of a BC_x film. This was used to qualitatively determine the composition and uniformity of the coating. However, BC_x films will be implanted with boron and oxygen of known amounts and then profiled so that quantitative measurements of the coating constituents can be made.

CONCLUSIONS

Boron-containing carbon coatings have been produced via a CVD reaction involving boron trichloride and benzene. XPS and NMR data support the hypothesis that the boron enters graphite as a substitutional impurity. X-ray diffraction showed that the BC_x film has a d_{002} approaching that of graphite and boron appears to induce a reordering of the carbon planes at relatively low temperatures. Raman spectroscopy showed that boron caused a shift of the graphitic peak to a lower frequency vibration due to the d_{002} of the BC_x film. SIMS confirmed elemental makeup and uniformity of the coating.

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