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CHARACTERIZATION OF NEWLY SYNTHESIZED NOVEL GRAPHITE FILMS

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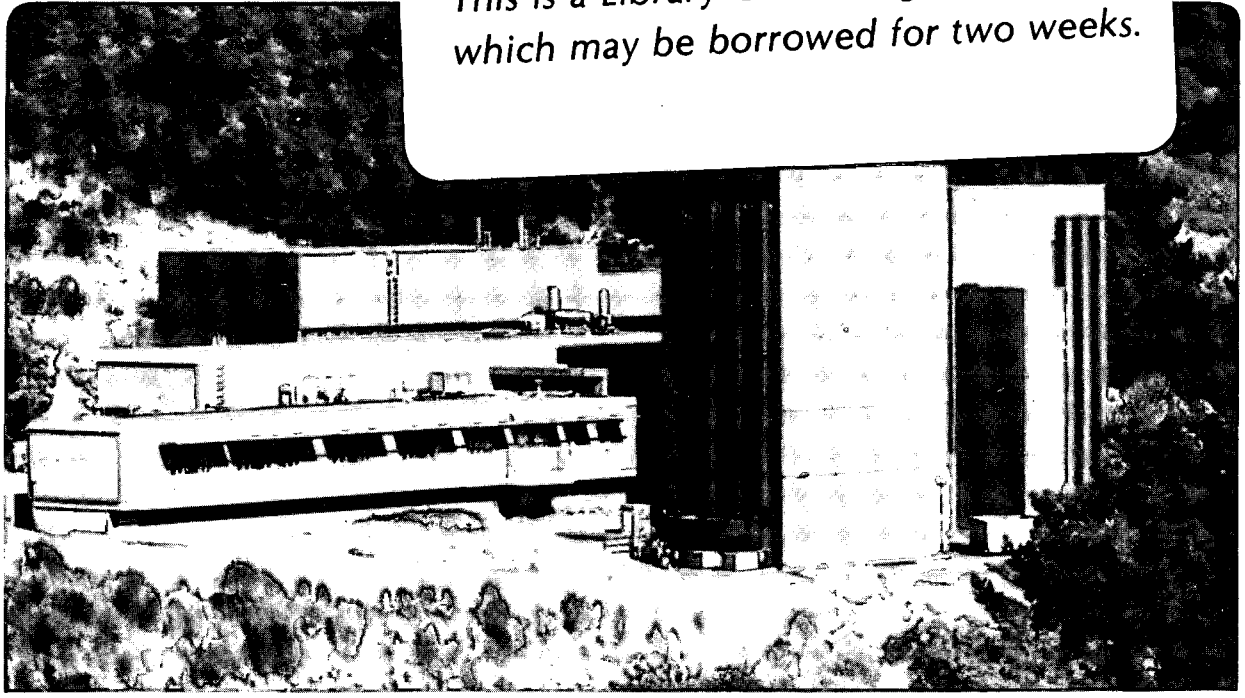**Characterization of Newly Synthesized
Novel Graphite Films**

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DISCLAIMER

CHARACTERIZATION OF NEWLY SYNTHESIZED NOVEL GRAPHITE FILMS

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ABSTRACT

Reactions of C_6H_6 and BCl_3 at 800°C yields a metallic graphite-like material of composition BC_x (3.0 ≤ x ≤ 4.00) while reactions of BCl_3, NH_3 and C_2H_2 produces a B/C/N graphitic semiconductor of approximate stoichiometry B_2CN_2. Both materials were shown to be homogeneous using Auger electron spectroscopy and extensively characterized by electron energy-loss spectroscopy. Single loss profiles of the EELS data were obtained using the fourier-log deconvolution method. Compositions were determined using hydrogenic cross-sections. A careful study of the plasmon resonance energies and the fine structures of the core-loss edges of these materials has been invaluable in demonstrating that the boron, carbon and nitrogen atoms are all sp^2 hybridized. Therefore, these new materials are in-sheet graphite hybrids and not intercalations.

INTRODUCTION

Even though graphite and boron nitride are isostructural with close dimensional relationship they have vastly different electronic properties. Graphite is a semimetal with a slight overlap of the valence and conduction bands, while the heteroatomicity of boron nitride results in it being an insulator with a band gap ≥ 3.8 eV. It is expected, therefore, that the addition of boron or nitrogen to graphite can not only help tailor-make the bandgap but also achieve much higher carrier concentration and mobility, provided that these elements substitute for carbon in graphite and do not form intercalations. However, it has been believed that the maximum substitution of boron in graphite, even at elevated temperatures, is less than 2.5 at%. Recently, effective low temperature routes for the synthesis of new boron/carbon and boron/carbon/nitrogen graphite hybrids have been developed [1,2]. These layered materials offer the possibility of making a whole range of novel junctions and devices in which the band gap and electrical conductivity are controlled, largely, by the composition and to some extent, by the particular atomic arrangement. Hence, a successful synthesis was achieved only by carrying it out in concert with effective, sensitive and appropriate characterization methods.

Electron-optical techniques, particularly electron energy-loss spectroscopy (EELS), using focussed high-energy incident electrons, has been invaluable in elucidating the composition, structure and bonding of these compounds [3]. The EELS technique is not affected by the poor sheet-to-sheet registry, observed in our samples, due to the low temperature non-epitaxial deposition process. This is unlike electron diffraction which does not reveal general hkl lines. EELS is a microstructure sensitive spectroscopic method and hence the small quantities of the material synthesized are sufficient for characterzation. This method is non-destructive and if used in low dose conditions does not destroy the true structure unlike XPS where the sputtering process used to clean the surface consistently ended up damaging the material. In this paper, details of the synthesis as well as the characterization of these newly synthesized films are presented.

SYNTHESIS

The synthesis of these novel graphites is readily carried out in a flow system on a heated substrate. B/C graphite is sheet-like with a metallic appearance and is formed by the interaction of benzene and boron trichloride at 800°C:

$$2BCl_3 + C_6H_6 \rightarrow 2BC_3 + 6HCl \tag{1}$$

In practice, it is observed [4] that the compound synthesized is non-stoichiometric BC_x, where x is related linearly to the substrate temperature and approaches stoichiometry (x=3) at temperature below 800°C.

The B/C/N graphites were synthesized using an hydrous ammonia (99.99%), boron trichloride (99.9%) and purified acetylene (99.6%), with nitrogen as a carrier gas to ensure the forward flow of the reactants, in a fused silica tube reactor heated by a clam-shell furnace. The overall reaction stoichiometry is approximately as follows:

$$xBCl_3 + y/2\ C_2H_2 + x\ NH_3 \rightarrow B_xC_yN_x + 3x\ HCl + y/2\ H_2 \tag{2}$$

The acetylene and boron trichloride were mixed before the introduction of ammonia in the hot zone to prevent the formation of ammonium chloride before the reaction zone.

EXPERIMENTAL DETAILS

Electron energy loss spectra were obtained using a Gatan 607 magnetic sector spectrometer attached to a JEOL 200 CX analytical electron microscope operating at 160 kV. Spectra were acquired in the image mode with an incident beam convergence angle of 9.0 mrads and a divergence angle of ~50 mrads (no objective aperture). The latter was to ensure accuracy in the Fourier-log deconvolution procedure which was ocasionally used to remove plural scattering effects. A small dose (1 mA, beam current) was used both to minimize damage to the sample as well as to obtain a good energy resolution ($\leq$ 2 eV, FWHM of the zero-loss peak). A variety of methods were used to prepare TEM specimens. The most successful procedure was to crush the films in an agate mortar and pestle and then to float the small particles onto holey carbon grids. Preliminary characterization by Auger electron spectroscopy, showed that the materials were homogeneous.

RESULTS & DISCUSSIONS

A typical EELS spectrum from these compounds, illustrating all the salient features (insets) is shown in Figure 1. The low-loss region ($\leq$ 50 eV) is dominated by the plasmon peak arising from the collective excitation of the outer electrons. Three features constitute the essential physics of plasmons : peak position, line width and the dispersion relation [5]. In the simplest "jellium" model, for a solid with a nearly-free electron gas of density n, the plasmon energy E_p is related to the density by $E_p = h\ \sqrt{4\pi ne^2/m}$. For layered compounds, such as BN and graphite, two prominent resonance peaks associated with the two groups of valence electrons (a π band lying close to the Fermi level and a σ band lying deeper) are observed. Ideally these features should occur (for graphite) at 12.5 and 25 eV, but in practice they are observed at 6.9 and 27.1 eV. These shifts are attributed to the "screening" of the plasmon resonance by the σ electrons [5]. Table I summarizes the plasmon peak positions of these newly synthesized graphites. Note that two distinct resonances, both π and $\pi + \sigma$, are observed in all cases. Further, the shift to lower energies of both BC_3 and $B_xC_yN_x$ plasmon energies, with respect to graphite and BN respectively is consistent with the reduction in electron density in these novel graphites. Finally, ignoring the "screening effects", if the free electron gas model is applied to calculate an effective valence electron density contributing to these oscillations, it can be seen that the ratio $n^{eff}(\sigma + \pi) / n^{eff}(\pi)$ of BC_3 and $B_xC_yN_x$ match those of graphite and BN respectively, showing that all these compounds are structurally similar.

TABLE I

Compound	Plasmon Energy (eV) π	σ + π	$\dfrac{n^{eff}\,(\sigma + \pi)}{n^{eff}\,(\pi)}$	π* edges (K-edge) B (eV)	C (eV)	N (eV)	σ* edges (K-edge) B (eV)	C (eV)	N (eV)
Graphite	6.9	27.1	15.43		284.0	-		290.0	-
BN	8.0	26.5	10.86	191.0	-	397.5	197.5	-	404.0
BC$_3$	6.4	24.8	15.21	188.5	282.5	-	195.0	290.5	-
B$_x$C$_y$N$_x$	7.5	24.5	10.70	190.5	284.0	398.0	197.5	290.5	404.0

The higher energy loss region ($50 \leq \Delta E \leq 1000$ eV) contains edges corresponding to the inner shell ionization of the elements constituting the material. The near edge fine structure of the core-loss edges for all the elements in graphite, BN, BC$_3$ and B$_x$C$_y$N$_x$, show prominent features corresponding to both π* and σ* antibonding levels corresponding to the unoccupied bound states of the conduction band. It can clearly be seen that all the elements in all these materials are sp^2 hybridized and occupy sites in the graphitic planes of the structure. Energy-loss edge values and their assignments are given in Table I while, the boron K-edge fine structure clearly illustrating the sp^2 character in all these compounds is shown in Fig. 2. Moreover, the energy values of the fine structure of the principal K-edges in these compounds can be matched with the band structure calculated at symmetry points of the Brillouin zone. In particular for BC$_3$, the equilibrium geometry and electronic structure have recently been calculated using the *ab initio* pseudopotential local orbital approach in the local density functional formalism [6]. The density of states for a monolayer of BC$_3$ clearly shows two distinct levels above the Fermi level separated by ~3 volts in very good agreement with the fine structure observed in the EEL spectra (Fig. 2). The structural model for BC$_3$ used in this calculation was a layered graphitic one, with every fourth carbon atom being substituted by boron.

Finally, the EEL spectra also provide for the elemental analysis of the new B/C and B/C/N graphites. The quantification formulae that are used are relatively straightforward and simple and require only a measurement of the integrated core-loss intensity over a particular energy window beyond the ionization edge and a calculated ionization cross section [5]. The ionization cross-sections used for our microanalysis was an approximate model based on hydrogen atom wavefunctions, with appropriate scaling to take into account the nuclear charge as well as screening effects [5]. It is estimated that the error in these analyses is of the order of 10-15 percent, largely due to the inaccuracy of the hydrogenic cross sections as well as the difficulty in modelling the strong background observed in an electron energy-loss spectrum. From our measurements, the composition of the two novel graphites were determined to be BC$_4$ and B$_2$CN$_2$. The deviation from the expected stoichiometry of the former compound is attributed to a greater pyrolization of carbon than is expected at this temperature.

In summary, novel graphitic thin films of boron, carbon and nitrogen have been synthesized by a chemical vapor deposition process using induction heated subtrates. Electron energy loss spectroscopy has been extensively used to characterize these materials and it has been shown that all the elements are sp^2 hybridized and substitute for carbon in the structure.

Fig. 1: Typical EEL spectrum from a sample of B/C/N graphite illustrating the fine structure in the principal core edges. The presence of prominent π^* and σ^* features confirms that all the elements are sp^2 hybridized and the material is truly graphitic.

Fig. 2: Details of the B-K edge in the newly synthesized B/C/N graphites. In B/C/N the considerable broadening that is observed can be attributed to the random distribution of boron. The 3 volt separation between the π^* and σ^* features in B/C graphite is in agreement with band structure calculations using a model where every fourth carbon is substituted by boron.
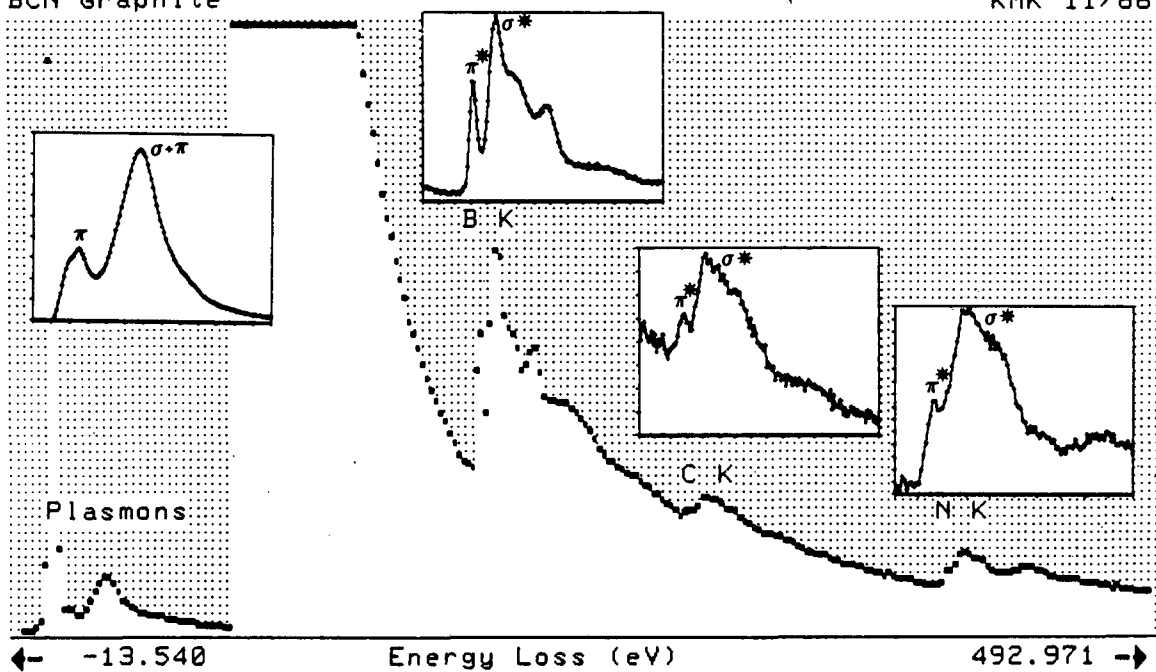
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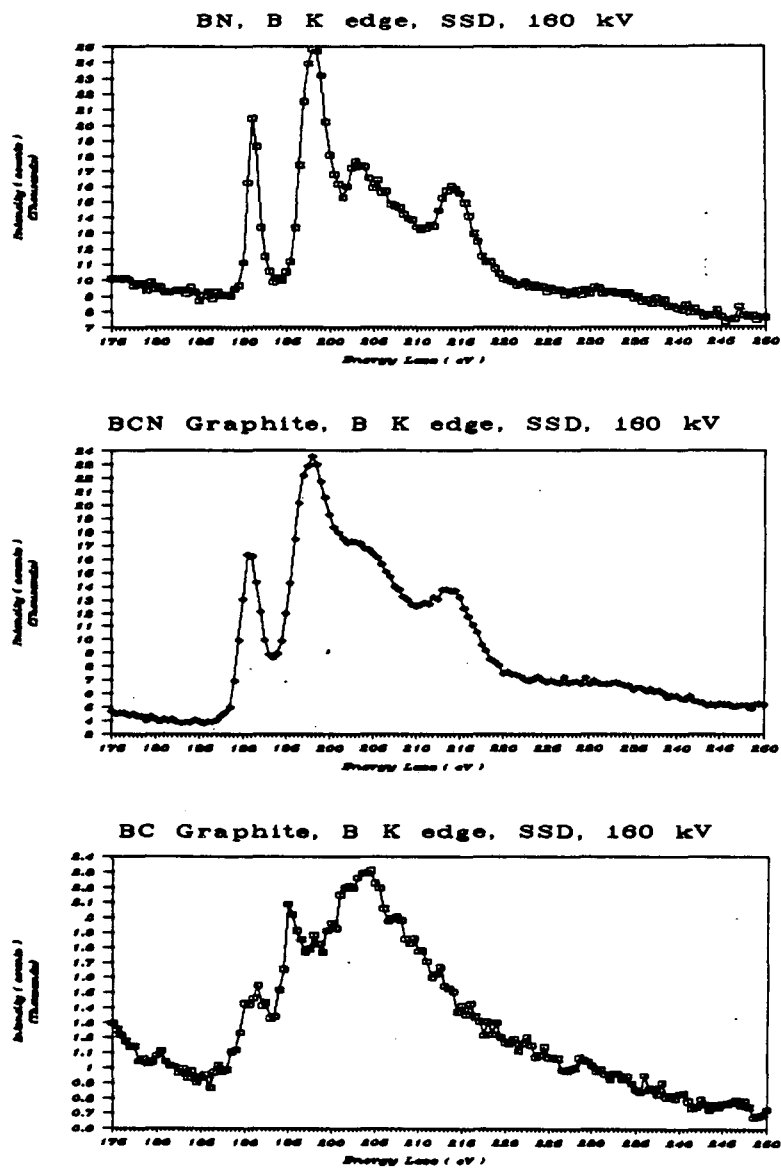6. D. Tomanek et al., (private communication).

Figure 1

BN, B K edge, SSD, 160 kV

BCN Graphite, B K edge, SSD, 160 kV

BC Graphite, B K edge, SSD, 160 kV

XBL 871-287

Figure 2