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# Band gap and chemically ordered domain structure of a graphene analogue $B_x C_y N_z$

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### ABSTRACT

Chemically synthesized few layer graphene analogues of  $B_x C_y N_z$  are characterized by aberration corrected transmission electron microscopy and high resolution electron energy loss spectroscopy (HREELS) to determine the local phase, electronic structure and band gap. HREELS band gap studies of a  $B_x C_y N_z$  composition reveal absorption edges at 2.08, 3.43 and 6.01 eV, indicating that the  $B_x C_y N_z$  structure may consist of domains of different compositions. The *K*-absorption edge energy position of the individual elements in  $B_x C_y N_z$  is determined and compared with h-BN and graphite. An understanding of these experimental findings is developed with complementary first-principles based calculations of the various ordered configurations of  $B_x C_y N_z$ .

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# 1. Introduction

The quest for new materials and an understanding of their properties has led to the extensive research in science and engineering of carbon nano-tubes and graphene [1–3]. With this motivation, the successful synthesis of graphene analogue materials out of various layered structures has been reported [4–8]. Among various graphene analogue materials,  $B_xC_yN_z$  attracts particular attention due to the tunability of its semiconducting band gap with control on its composition. Graphene is a semimetal whereas BN is an insulator.  $B_xC_yN_z$ , an intermediate mixture with composition of graphene and BN, possesses direct band gap semiconducting properties depending on its atomic proportions (*x*, *y*, *z*) and ordering. Many novel electronic device applications can be realized by utilizing this new class of materials.

 $B_x C_y N_z$  in the two dimensional nano-structure and in other forms is highly stable and particular interest exists in determining the arrangement of its atoms or phases and their relationship with electronic structures. Theoretically, many configurations of hexagonal BCN with comparable energies (within 1%) have been predicted, and those consisting of motifs with BN<sub>3</sub> interlinked with NB<sub>3</sub> are found to have the lowest energy [4]. The electronic structure was also reported for BC<sub>2</sub>N in the single layer compound for various motifs and the lowest energy structure was found to be a semiconductor with a gap of ~1.61 eV [9]. Experimentally, XPS study provides information on the identification of the bonds between elements but this is based on curve fitting of the absorption peak and only suggestive about the formation of any possible phases. EELS quantification very accurately provides the relative amounts of individual elements in a very small area and this information can only approximate in suggesting the formation of a particular phase. For example, EELS guantification cannot provide information on whether there is a homogeneous distribution of B, C, and N atoms or whether the  $B_x C_y N_z$  layer structure is a mixture between graphene and BN. Electron energy loss near edge structure (ELNES) up to 50 eV energy loss from the core absorption edge in a transmission electron microscope has the capability to provide finger printing on the coordination along with high spatial resolution, but due to the unavailability of standards it has not been possible to correlate the energy loss spectra with the exact nature of phases formed in  $B_x C_y N_z$ . There was another report on the theoretical computation of the EEL near edge spectra of BCN [10]. The calculation was based on single electron molecular orbital theory. The EELS spectra for h-BN, BC<sub>2</sub>N, BC<sub>3</sub> can serve as guides to compare the experimental spectra of a given  $B_x C_y N_z$ composition. Recently, the formation of nano size domains of C doped h-BN and graphene has been reported based on UV absorption spectra for  $B_x C_y N_z$  grown by CVD [11]. Here we report the experimental determination of band gap edge absorption by high resolution EELS using a gun monochromator and compare with the first-principles pseudopotential based density functional theory (DFT) calculations of BCN, BC<sub>2</sub>N and BCN<sub>2</sub> with various motifs to understand and predict the presence of phases in a



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Fig. 1. Electron energy loss near edge structures for both BCN and BN at the (a) B K and (b) N K edge. Extra features are marked by A/B at the B K edge structure.

chemically synthesized  $B_x C_y N_z$  composition. The experimental electron energy loss near edge structure and *K*-edge energy absorption values of the  $B_x C_y N_z$  sample are reported and the latter are interpreted through comparison with h-BN layer structure and graphite.

#### 2. Experiment

Graphene analogues of  $B_x C_y N_z$  and BN were synthesized by chemical synthesis route using a mixture of urea, boric acid and activated charcoal for  $B_x C_y N_z$ , urea and boric acid for BN. The mixture was then heated at  $\sim 900$  °C [4]. The formation of a number of layers can be controlled by controlling the amount of urea in the reaction mixture and it was found that the number of layers decreases with the increasing amount of urea in the mixture [6]. The EELS data of BN is also presented to compare with the  $B_x C_v N_z$ . HRTEM imaging was performed in an aberration corrected FEI TITAN<sup>3™</sup> 80–300 kV microscope. The images were acquired under a negative spherical aberration coefficient  $(C_s)$  of about 30  $\mu$ m along with a small positive defocus ( $\Delta f$ ) value of about 8 nm (bright atom image). The band gap absorption and electron energy loss near edge structure study were performed using a gun monochromator at 300 kV with an energy resolution better than 0.2 eV (measured from FWHM of zero loss peak). The K-edge absorption energy for various elements was determined by calibrating the spectra with respect to the zero loss peak position.

#### 3. Results and discussion

Transmission electron microscopy images have already confirmed the formation of a few layers of  $B_x C_y N_z$  and BN and the hexagonal arrangement of atoms [4,5]. Although it is now possible to characterize a few layers of BN [12] and similar materials by atomic resolution phase contrast imaging, for chemically synthesized buckled sample atomic resolution imaging is very difficult. As mentioned before, XPS is routinely employed to deduce the nature of chemical bonding environments between the elements in BCN by a peak fitting procedure of the absorption edge. Mannan et al. [13] reported the formation of B-N, B-C, C-C, N-C types of bonding in their BCN film produced by microwave plasma CVD. From XPS, the presence of four different sp<sup>2</sup> hybrid configurations (BN<sub>3</sub>, BN<sub>2</sub>C, BNC<sub>2</sub>, BC<sub>3</sub>) around the B atom was suggested. XPS study of our sample revealed close to equal distribution of the elements in  $B_x C_v N_z$  [4]. We have used high resolution EELS for determining accurately the K-edge absorption energy value for different elements of two dimensional layers both in  $B_x C_y N_z$  and BN. Table 1 summarizes the absorption edge energy positions for both  $\pi^*$  and  $\sigma^*$  absorption edges. The B  $\pi^*K$  edge of BCN appears at  $\sim$ 188.9 eV whereas for BN it is at  $\sim$ 190.9. Similarly, the N  $\pi^*$ K edge

# Table 1

Experimental K absorption edge energy positions of a few layers  $B_x C_y N_z$  and BN determined by high resolution EELS.

K edge energy	BCN (eV)	BN (eV)
BK $(\pi^*)$	188.91	190.86
N K $(\pi^*)$	397	401.53
$CK(\pi^*)$	280.20	-
$BK(\sigma^*)$	195.20	197.61
NK $(\sigma^*)$	403.16	408.67
$CK(\sigma^*)$	287.80	-

Table 2

EELS quantification and possible phase formation in the structure from different areas.

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Area	EELS quantification	Possible phases
A1	B <sub>3.3</sub> CN <sub>5.8</sub>	Domains of BN and low C doped BN
A2	B <sub>0.9</sub> CN <sub>1.8</sub>	Mostly low C doped BN
A3	B <sub>0.9</sub> CN <sub>1.8</sub>	Mostly low C doped BN
A4	B <sub>2.8</sub> CN <sub>4.0</sub>	Domains of BN and low C doped BN
A5	B <sub>2.9</sub> CN <sub>6.2</sub>	Domains of BN and low C doped BN
A6	B <sub>1.6</sub> CN <sub>1.9</sub>	Mostly low C doped BN

for BCN is ~397.0 eV and for BN it is ~401.5 eV. The carbon *K* edge for BCN is determined to be 280.2 eV and this value for graphite is 284.3 eV. These results suggest that this  $B_x C_y N_z$  sample is different from h-BN and graphite. However, we are unable to predict the formation of different phases present in the sample. Our absorption edge value for BN is a little different from literature BN values (191.4 and 398.9 eV for B and N respectively) and the reason is the reduced dimension in one direction compared to the bulk form of BN [10]. The separation between  $\pi^*$  and  $\sigma^*$  of the B *K* and N *K* edge was found to be the same (7.2 and 6.3 eV respectively) for both BCN and BN.

EELS quantification was carried out to find the elemental distribution and average composition of  $B_x C_y N_z$ . We found either C deficient some form of  $B_x C_y N_z$  in most of the regions or almost equal proportions of  $B_x C_y N_z$  in some areas. Table 2 lists the composition data from different regions of samples and approximate average chemical phases. It seems that we have the BCN<sub>2</sub> phase in many areas. However, the presence of band edge absorption in low loss EEL spectra rules out the presence of any BCN<sub>2</sub> phase after comparing with theoretical calculations and is discussed later.

The EEL spectra show strong  $\pi^*$  peaks apart from  $\sigma^*$  which is a signature of a two dimensional graphene-like hexagonal structure (sp<sup>2</sup> hybridization). The EELS near edge structure provides information about the density of unoccupied states in the conduction band and is very useful to get information about coordination fingerprinting. One can note the difference in the near edge structure between  $B_x C_v N_z$  and BN in Fig. 1. The peak



Fig. 2. Band gap absorption edges at 2.25, 3.35 and 6.01 eV showing the formation of domain structure in BCN.

A/B is more pronounced/weak in  $B_x C_y N_z$  compared to BN. No clear difference is observed for the N K near edge structure.

We have performed a band gap absorption edge measurement using high resolution EELS. A gun monochromator with a resolution better than 0.18 eV was used to determine the band edge absorption in our chemically synthesized samples. Theoretical calculation predicted the direct band gap energy of 1.8 eV for BCN with interlinked BN3 and NB3 motifs, which has the lowest energy structure. We have obtained the band edge absorption energy (measured at midpoint of the edge, see Fig. 2) at 2.08 ( $\pm$ 0.2), 3.43 ( $\pm$ 0.2) and 6.01 eV in most of the regions. This suggests that the sample consists of domains of h-BN and two different types of slightly C-doped h-BN with little N rich condition. Therefore one could decompose the atomic percentage obtained by EELS guantification into combinations of h-BN and two different levels of C doped h-BN domain structure. This further confirms the nature of the  $B_x C_y N_z$  two dimensional layers consisting of domains of different compositions. The composition of domains may be dependent on the synthesis route.

We have used plane wave self consistent field (PWSCF) implementation of density functional theory (DFT) [14], with a generalized gradient approximation (GGA) [15] to exchange the correlation energy of electrons and ultrasoft pseudopotentials [16] to represent the interaction between the ionic cores and valence electrons. We determine the electronic band structure for various possible phases of monolayer  $B_xC_yN_z$ , namely BCN, BC<sub>2</sub>N and BCN<sub>2</sub> with different atomic configurations (or motifs). Kohn–Sham wave functions were represented with a plane wave basis with an energy cutoff of 25 Ry and charge density with a cutoff of



Calculated band gap energy and stability of the  $BC_2N$  phase for various motif configurations.

Structure of BC <sub>2</sub> N	Lattice constant (Å)	E <sub>cohesive</sub> (eV/atom)	Band gap (eV)
1	5.01	8.28	1.95
2	5.02	8.37	Metallic
3	5.01	8.58	1.45
4	5.02	8.31	0.55
5	5.02	8.05	0.46

Table 4

Calculated band gap energy and stability of the BCN<sub>2</sub> phase for various motif configurations.

Structure of BCN <sub>2</sub>	Lattice constant (Å)	E <sub>cohesive</sub> (eV/atom)	Band gap (eV)
1	4.94	7.93	Metallic
2	4.94	7.95	Metallic
3	5.02	7.34	Metallic
4	4.94	7.86	Metallic
5	5.03	7.56	Metallic

150 Ry. A monolayer with an eight atom unit cell was considered in the calculation. Integration over the Brillouin zone was sampled with a Monkhorst–Pack scheme [17] with a  $12 \times 15 \times 1$  mesh of k points and the occupation numbers were smeared using a Methfessel-Paxton scheme [18] with a broadening of 0.01 Ry. The structures are allowed to relax fully to minimize energy until the force on each atom is less than 0.001 Ry/bohr. The lattice constants of five different configurations (see Fig. 3) vary within 1% of each other and the smallest one is 5.01 Å for BC<sub>2</sub>N and 4.94 Å for BCN<sub>2</sub>. The details of the BCN structure have been reported earlier [4]. The cohesive energy of the lowest energy structure for BC<sub>2</sub>N is 8.58 eV/atom and that of BCN<sub>2</sub> is 7.95 eV/atom, which are smaller than BCN (8.61 eV/atom), graphene (9.16 eV/atom) and BC<sub>4</sub>N (8.93 eV/atom). The cohesive energies of other structural arrangements of BC<sub>2</sub>N and BCN<sub>2</sub> are given in the Tables 3 and 4. The most stable structures of BCN and BC<sub>2</sub>N are semiconductors with band gap energies of 1.8 eV and 1.45 eV respectively. For five different configurations, BCN<sub>2</sub> appeared to be metallic which is due to the presence of extra N atoms and elements in the structure. Fig. 4 shows the electronic density of states of BC<sub>2</sub>N and BCN<sub>2</sub> for the lowest energy configurations, indicating their semiconducting and metallic characteristics. These calculations helped us in ruling out the formation of any BCN<sub>2</sub> phase in the BCN alloy and confirming the domain structure from both band gap absorption edge measurement and EELS quantification.



Fig. 3. Various atomic configurations of (a) BC<sub>2</sub>N, and (b) BCN<sub>2</sub>.



Fig. 4. DOS of BC<sub>2</sub>N and BCN<sub>2</sub> for the lowest energy configuration.

# 4. Conclusions

In summary, we have shown from the band gap absorption edge that h-BN and two different low C doped h-BN phases have been formed in a  $B_x C_y N_z$  sample synthesized by a chemical route. Band gap values of 2.03 eV and 3.43 eV have been obtained for two low C doped h-BN domains. The K-edge energy absorption values indicate that bonding between the atomic pairs of B, C and N has been formed.

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