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Synthesis of a new boron carbonitride with a B_4C-like structure from the thermolysis of *N*-alkylated borazines

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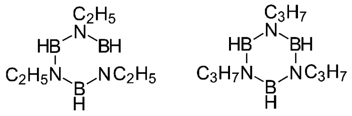
Thermolysis of *N*-trialkyl borazines at 500 °C produces homogeneous, amorphous boron carbonitride phases, whose compositions are dependent upon the borazine substituent, and whose structures are similar to that of icosahedral boron carbide, B_4C.

There is considerable current interest in coatings containing boron, carbon and nitrogen (boron carbonitride, BCN)[1] because of the likelihood that, like diamond, cubic boron nitride (c-BN) and carbonitride (β-C_3N_4), they will possess excellent mechanical properties such as hardness and resistance to heat, wear and corrosion.[2]

Boron nitride films have been obtained by chemical vapour deposition utilising both borazine ($H_3B_3N_3H_3$)[3] and borazine derivatives.[4] However, the production of boron carbonitrides from carbon-containing borazine derivatives has received very little attention. The only published examples involve the production of a boron carbonitride from *B*-trichloroborazine *via* a sol–gel route[5] and four independent reports of thermolyses of borazine derivatives, all of which resulted in the formation of materials which were found to be phase separated into crystalline boron nitride and a partially crystalline (graphitic) carbon phase.[1,6,7] It is unsurprising that, in the majority of cases, the materials produced from borazines are hexagonal phases similar in structure to graphite.[8] During the conversion of the precursor to the ceramic product, the ring system is generally preserved.

Work in our laboratories on the thermolysis of *N*-alkylated borazines has produced amorphous boron carbonitride phases which do not adopt the expected graphitic structure. The precursors, *N*-triethylborazine ($(C_2H_5)_3N_3B_3H_3$) **1** and *N*-tripropylborazine ($(C_3H_7)_3N_3B_3H_3$) **2** (Fig. 1), are easily prepared by the reaction of diborane with CH_3CN and CH_3CH_2CN respectively.[9] Gas-phase thermolysis of these compounds at 500 °C under high-vacuum conditions (*ca.* 10^{-6} torr) results in the deposition, on quartz discs, of adhesive brown films with negligible oxygen contents.

X-Ray powder diffraction showed no evidence for the presence of crystalline material, and this was confirmed by selected area electron diffraction (SAED) in the transmission electron microscope (TEM) which, in all cases, revealed broad, diffuse rings characteristic of amorphous material. There were no signs of 'graphitic' reflections. The nature of the bonding within the films was studied by X-ray photoelectron spectroscopy (XPS). The component peak positions and relative intensities from the deconvoluted spectra are given in Table 1 and have been charge-corrected by referencing to the peak due to surface hydrocarbon contaminants at 284.6 eV. By comparison with a range of literature data, the present results strongly suggest the presence of both B–N and B–C bonds in both samples. The boron–carbon bonding appears to be similar to that found in cubic boron carbides (*i.e.* sp^2 and sp^3) rather than that in boron-substituted graphites (sp^2 only).



1 **2**

Fig. 1 Borazine precursors used in this study.

TEM samples were prepared by scraping the coatings off the silica substrate and dispersing onto holey carbon-coated grids. Electron energy loss spectroscopy (EELS) and particularly energy loss near-edge structure (ELNES) provide information about the local site and symmetry-projected unoccupied density of electronic states (DOS) in a material, which is very sensitive to the local structure and bonding associated with the atom undergoing ionization. Both the B K- and C K-ELNES spectra recorded from the films produced from both *N*-triethylborazine and *N*-tripropylborazine were very similar to the spectra obtained from crystalline B_4C – both in terms of the absolute energy onset and overall shape. This suggests that both materials consist of icosahedral clusters of atoms. The B K-ELNES and C K-ELNES spectra of the materials produced in this study are shown in Fig. 2(a and b). The B K-ELNES spectra of crystalline hexagonal-BN and B_4C, as well as the C K-ELNES of B_4C and partially crystalline graphite (heat treated at 1023 K) are included for comparison, and agree well with literature data.[7,18]

EELS spectra from a number of different specimen areas (approximately 100 nm in diameter) in each sample were quantified using standard procedures and hydrogenic cross-sections. Within each of the two samples, the composition was found to vary very little from area to area, demonstrating that the materials consist of single homogeneous BCN phases, at least on the sub-micron scale. This was confirmed by means of nanometre resolution energy-filtered TEM using a Gatan Imaging Filter, where boron K-, carbon K- and nitrogen K-edge EELS elemental maps all showed no evidence for elemental segregation. The average composition of the *N*-triethylborazine-derived material was determined to be $BC_{0.42}N_{0.27}$, and

Table 1 Charge corrected peak energies from the deconvoluted narrow-scan XPS spectra on thin films deposited from precursors **1**–**2** and comparison with literature values

	Binding energy[a]/eV	Literature comparison/eV	Ref.
Film from thermolysis of **1**			
B 1s	188.6 [93%]	B–C bonding (188.5)	10
B 1s	191.2 [7%]	N–B–C bonding (191.4)	11
C 1s	282.5 [64%]	B–C bonding in B_4C (282.5)	12
C 1s	283.8 [36%]	B–C bonding in B_4C (283.7)	13
N 1s	397.5 [100%]	B–N bonding (397.6)	12
Film from thermolysis of **2**			
B 1s	189.6 [94%]	B–C bonding (189.6)	11
B 1s	192.0 [6%]	BCO_2 (192.0)	14
C 1s	282.7 [7%]	B–C bonding in B_4C (282.5)	12
C 1s	283.4 [88%]	B–C bonding in B_4C (283.7)	13
C 1s	285.9 [5%]	Partial oxidation	
N 1s	398.1 [92%]	B–N bonding (398.0)	15
N 1s	399.8 [8%]	CN (aromatic) (399.5) or NH_2 (399.4)	16

[a] Figures in parentheses indicate the percentage contribution to the composite peak from the particular component.

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that of the *N*-triethylborazine-derived material was $BC_{0.64}N_{0.31}$. In both materials, oxygen contents as determined by EELS were less than a few atom percent, in broad agreement with XPS results (from XPS the oxygen contents were 4.7 and 2.9% for films **1** and **2**, respectively). Thus it would appear that the elemental composition of the material is directly related to that of the precursor—with some preferential loss of carbon and nitrogen, possibly as alkyl amines or cyanides.

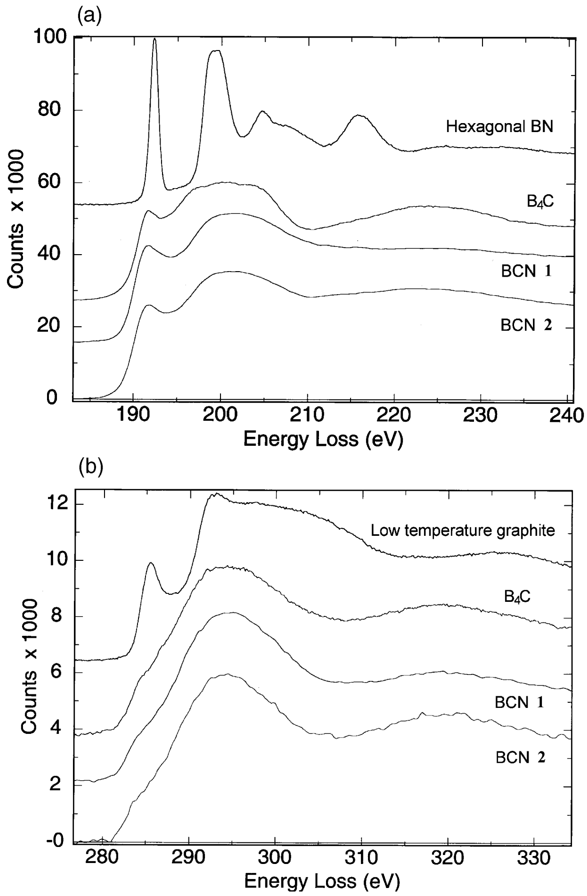

Fig. 2 (a) ELNES B K-edge spectra of the materials produced from precursors **1** and **2**. Spectra of crystalline h-BN and B_4C are included for comparison. (b) ELNES C K-edge spectra of the materials produced from precursors **1** and **2**. Spectra of partially crystalline graphite and B_4C are included for comparison. Electron energy loss spectroscopy (EELS) conducted in a 200 kV transmission electron microscope (TEM) was used to determine the composition of the films, and, by examination of the energy loss near-edge structure (ELNES), to investigate their electronic structures[17] and so confirm the findings from XPS.

We believe this to be the first example of the preparation of a single-phase boron carbonitride from a substituted borazine precursor. We also believe this to be the first reported instance of the gas-phase thermolysis of a borazine-based precursor in which the ceramic product does not retain any ring systems in its structure.

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