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Evidence for multiple polytypes of semiconducting boron carbide (C_2B_{10}) from electronic structure

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Abstract

Boron carbides fabricated via plasma enhanced chemical vapor deposition from different isomeric source compounds with the same $C_2B_{10}H_{12}$ closo-icosahedral structure result in materials with very different direct (optical) band gaps. This provides compelling evidence for the existence of multiple polytypes of C_2B_{10} boron carbide and is consistent with electron diffraction results.

The electronic structure of the semiconductor material based on the packing of icosahedra is quite complex [1–5] and far from completely mapped in detail. Nonetheless, the consensus is that the building block of all these materials is based on the icosahedron [1–11]. There are very strong indications from electronic structure studies [5, 12, 13] that there are several polytypes for the “ C_2B_{10} ” material. This is an added complication. The evidence for multiple polytypes of boron carbide has become more compelling with the discovery that weakly p-type and n-type boron carbide semiconductor materials are formed following plasma enhanced chemical vapor deposition (PECVD) [13] or synchrotron radiation assisted decomposition [13, 14] of the source compounds *ortho*-carborane (*closo*-1,2-dicarbadodecaborane) and *meta*-carborane (*closo*-1,7-dicarbadodecaborane), respectively (whose molecular structures are shown schematically in Figure 1). We have extended these studies to *para*-carborane (*closo*-1,12-dicarbadodecaborane) and have found a significant variation in the direct valence band edge to conduction band edge gap leading us to believe that multiple polytypes of boron carbide close to C_2B_{10} stoichiometry must exist.

We have grown semiconducting boron carbide on a variety of substrates by PECVD in custom 13.56 MHz radio frequency parallel plate reactors, as described previously [5, 15]. In order to characterize the optical properties of the semiconducting boron carbide films, the absorbance and reflectance of the samples were determined using a Perkin-Elmer Lambda 900 spectrometer equipped with a Pella 8006 specular reflectance accessory. This spectrometer is calibrated for direct measurement of absorbance over the photon energy range of 0.5–5 eV necessary for this study. We have undertaken absorbance measurements in both transmission and reflectance. The transmission measurements were taken both prior and post deposition so that the absorbance due to the quartz substrate could be subtracted. For the electron beam diffraction studies, the films were removed from the Si substrates, on which they were grown, and mounted on Cu mesh grids for transmission electron microscopy (TEM) study and were left on their substrates for x-ray diffraction characterization [15, 16].

The ground state theoretical model calculations of the three isomeric carboranes were undertaken with the HyperChem package using PM3-NDO (neglected differential overlap) calculations with the PM3 basis set [17].

These semi-empirical model calculations of the electronic structure were performed following geometry optimization and the lowest restricted Hartree-Fock (RHF) energy states. The state symmetries (the irreducible representations) were also determined. As seen in Figure 1, the *ortho*-carborane (*closo*-1,2-dicarbadoecaborane), *meta*-carborane (*closo*-1,7-dicarbadoecaborane), and *para*-carborane (*closo*-1,12-dicarbadoecaborane) are isoelectronic with very similar electronic structure as noted elsewhere [14, 18]. We have obtained highest occupied (HOMO) to lowest unoccupied (LUMO) molecular orbital gaps of 10.1 eV, 10.7 eV, and 10.0 eV for *ortho*-carborane, *meta*-carborane, and *para*-carborane, respectively, from our model calculations, as seen in Figure 1. This is very similar to our previous results of a 10.9 eV HOMO-LUMO gap obtained for *ortho*-carborane and *meta*-carborane obtained from MNDO [7, 18]. While it is widely believed that the synchrotron radiation or plasma assisted decomposition process forms the boron carbide semiconductor by dehydrogenation of the icosahedral molecule [14, 15, 19], this does not account for direct and indirect bonding between adjacent icosahedra, the relative orientation between icosahedra or the packing mode. Even for adsorption of the intact molecule there are clearly solid state interactions that, surprisingly, are sufficient to lead to shifts in the chemical potential [14, 18] so that a condensed film of molecular *meta*-carborane is more "n-type" in appearance than a film of condensed molecular *ortho*-carborane.

As expected, dehydrogenation results in a closing of the HOMO-LUMO gap, as seen in Figure 1, where we have plotted the molecular orbitals near the chemical potential for the fully hydrogenated species (12 hydrogens, except in the case of $\text{PCB}_{10}\text{H}_{11}$), the partly dehydrogenated species (6 hydrogens) and the completely dehydrogenated species (no hydrogens). Complete dehydrogenation, although providing a smaller HOMO-LUMO gap of 6.52 eV, 7.55 eV, and 6.56 eV for the symmetry restricted *ortho*-carborane, *meta*-carborane, and *para*-carborane, respectively, fails to provide an indication of the direct band gap of the solid semiconducting boron carbide.

Although these molecular calculations suggest that the relative placement of the carbon atoms within the cage have little effect on the band gap, some differences are observed in experiment, as discussed below. Variations in the experimental band gap, in deposited boron carbide films, arise through differences in packing of adjacent icosahedra either through differing relative orientation of adjacent icosahedra or through differences in direct or indirect (linkage) bonding. In addition, differences in the extent of dehydrogenation of the precursor molecule(s) could clearly affect the resulting boron carbide band gap.

The direct band gap is readily evident from the absorbance of the boron carbide films, obtained in transmission, as well as from plots of $(\alpha h\nu)^2$ of the transmission, as indicated in Figure 2. These Tauc plots [20], of the transmission optical properties, provide values for the valence band edge to conduction band edge gap that are similar to the values we estimate from the reflectivity measurements. By assuming that for small reflectivity the absorbance is proportional to the absorption α , for fixed film thickness, we

have estimated the direct band gap in our boron carbide samples using the formulation by Moss [21]:

$$\alpha \propto (h\nu - E_g)^{1/2} \quad (1)$$

and constructing a Tauc plot [20] of $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, as shown in Figure 3.

The direct band gaps (Figures 2 and 3) obtained from the optical measurements for the boron carbides fabricated from the source compounds of *ortho*-carborane (1.5 ± 0.2 eV) and *meta*-carborane (1.3 ± 0.2 eV) afford reasonable

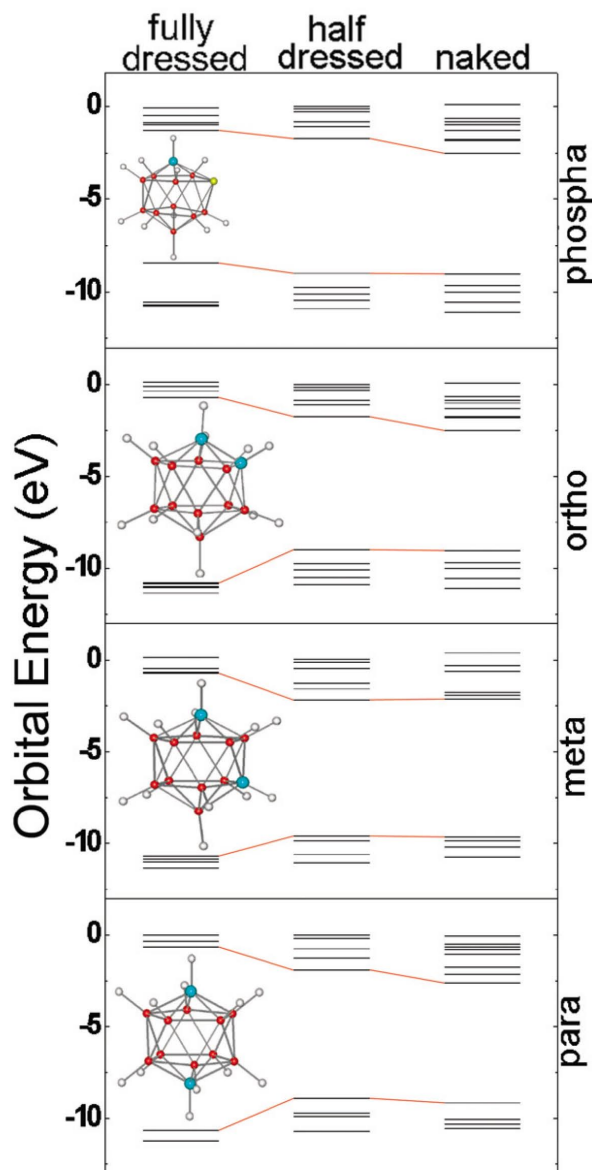


Figure 1. Theoretical calculations of HOMO-LUMO gap as a function of dehydrogenation for isolated *closo*-1-phospha-2-carbaundecaborane ($\text{PCB}_{10}\text{H}_{11}$), *ortho*-carborane, *meta*-carborane and *para*-carborane, i.e. fully hydrogenated (dressed), partially dehydrogenated to only six hydrogens (half dressed) and fully dehydrogenated. The fully hydrogenated molecules are shown as insets. The boron atoms are indicated in red, the carbon atoms in blue and the phosphorus atom (in the case of the phospha-carborane) in yellow.

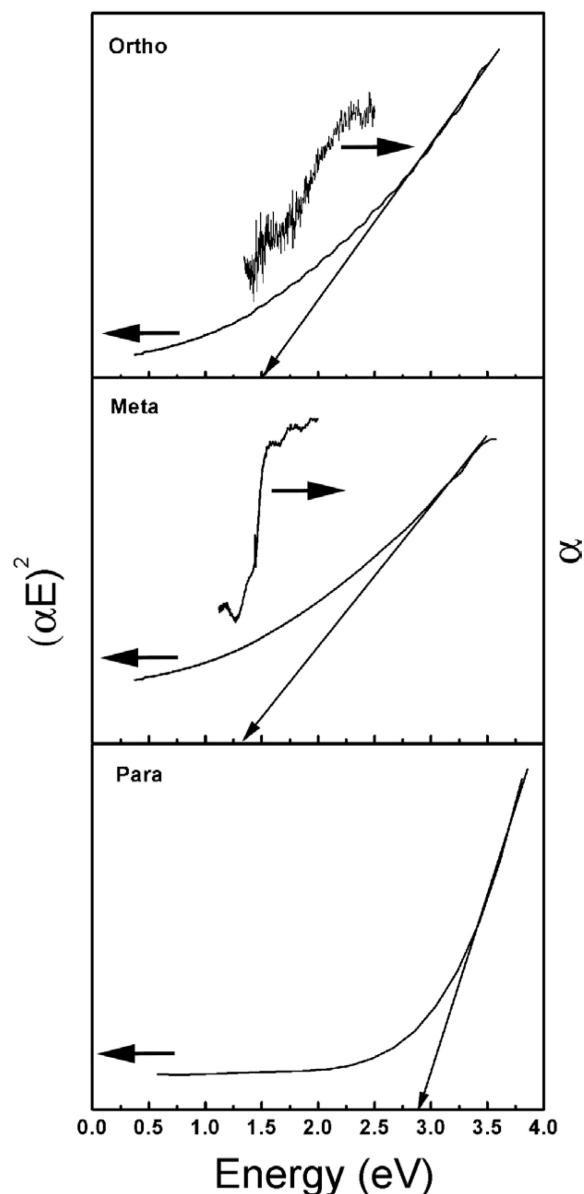


Figure 2. The direct band gaps derived from the transmission optical properties of “ C_2B_{10} ” boron carbides fabricated by PECVD from *ortho*-carborane, *meta*-carborane, and *para*-carborane. The absorbance for *ortho*-carborane and *meta*-carborane also provide some indications of the onset of the band gap, in addition to the direct band gap derived from the appropriate Tauc plots.

agreement with values of the direct band gap previously obtained from the semiconducting boron carbide formed from the *ortho*-carborane source compound (1.25 eV [22]) and the $B_{50}C$ boron carbide (2.1 eV [5]). Small variations in the magnitude of the band gaps due to residual hydrogen in the semiconducting boron carbide film [5] cannot be excluded, and indeed may be likely. Nonetheless, it is abundantly clear that the boron carbide formed from *para*-carborane has a much larger direct band gap of 2.75 ± 0.2 eV, as seen in Figures 2 and 3, than the material formed with either *ortho*-carborane or *meta*-carborane as the source compound.

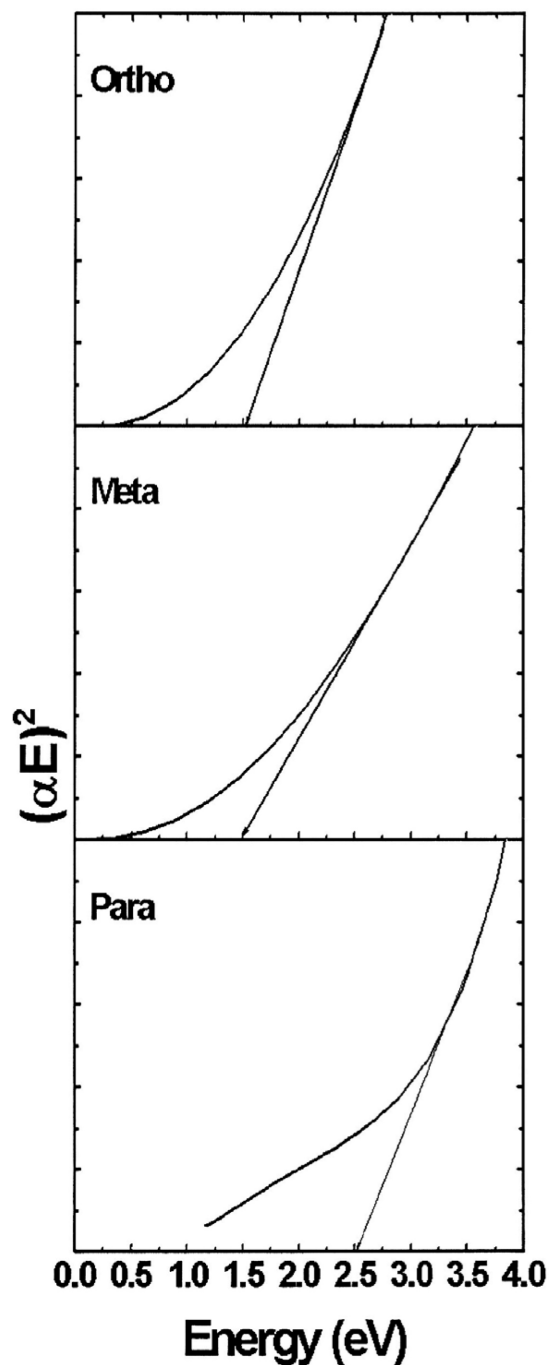


Figure 3. The direct band gaps derived from the reflectance optical properties of “ C_2B_{10} ” boron carbides fabricated by PECVD from *ortho*-carborane, *meta*-carborane, and *para*-carborane.

This value of 2.75 ± 0.2 eV for a direct band gap of a C_2B_{10} semiconducting boron carbide is very close to the 2.6 eV *indirect* band gap obtained for the C_2B_{10} semiconducting boron carbide containing less than 3% phosphorus formed by PECVD from the single source compound dimeric phosphorus bridged *ortho*-carborane $(C_2B_{10}H_{10}PCl)_2$ [12], as seen in Figure 4. This latter boron carbide has a direct band gap of about 3.75 eV. This large band gap material is also nominally C_2B_{10} but contains small amounts of hydrogen and phosphorus [12]. The position of the phosphorus is uncertain, but clearly the large band gap cannot be explained by

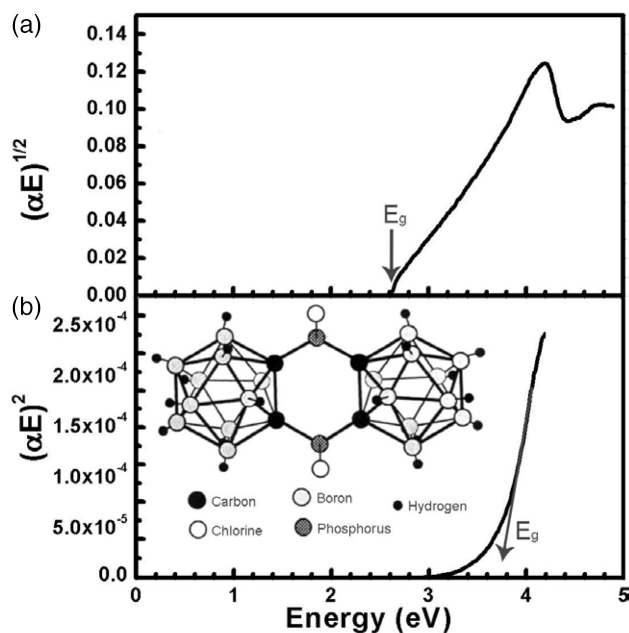


Figure 4. The optical properties of “ C_2B_{10} ” boron carbide containing 3% phosphorus formed from the decomposition of dimeric chloro-phospha(III)-carborane, shown as an inset. The indirect band gap (a) and direct band gap (b) are derived from the appropriate Tauc plots.

simple phosphorus inclusion in the icosahedral cage alone. First, the phosphorus content is far too small (<3% phosphorus) [12] and second, even if there were sufficient phosphorus for inclusion in every icosahedral cage, the dehydrogenated isolated *closo*-1-phospha-2-carbaundecaborane ($PCB_{10}H_{11}$) shows a HOMO–LUMO gap that differs little from the other *molecular dehydrogenated* carboranes (6.83 eV), as seen in Figure 1. Indeed this phosphacarborane molecule exhibits a HOMO–LUMO gap that is smaller than the other carboranes in the fully hydrogenated molecule (8.27 eV) (Figure 1).

There is other evidence of multiple polytypes, of the C_2B_{10} boron carbides, from electron beam diffraction, as seen in Figure 5. The material grown from *closo*-1,2-dicarbadoecaborane (*ortho*-carborane) is routinely nanocrystalline or amorphous with small areas of crystallinity, as evidenced by peaks in x-ray diffraction patterns [5, 16] and by spots and fringes in electron diffraction patterns and images [23]. The structure of the films is quite stable under annealing at 800°C and under argon ion bombardment when the films are still attached to their substrates. However, we have found that the microstructure of TEM grid-mounted boron carbide films bombarded by 5.4 keV argon ions does change considerably. The high energy argon ion bombardment results in substantial grain growth, at the very least, as evidenced by the narrowing of the ring widths (Figure 5). The rings of diffraction spots in the selected area diffraction pattern in Figure 5(b) are well defined, corresponding to crystal grain sizes of order 10 nm and larger. Upon bombardment, it may well be that there is also change in the cross-linking of icosahedra. These samples may not comprise a simple stacking of identically re-

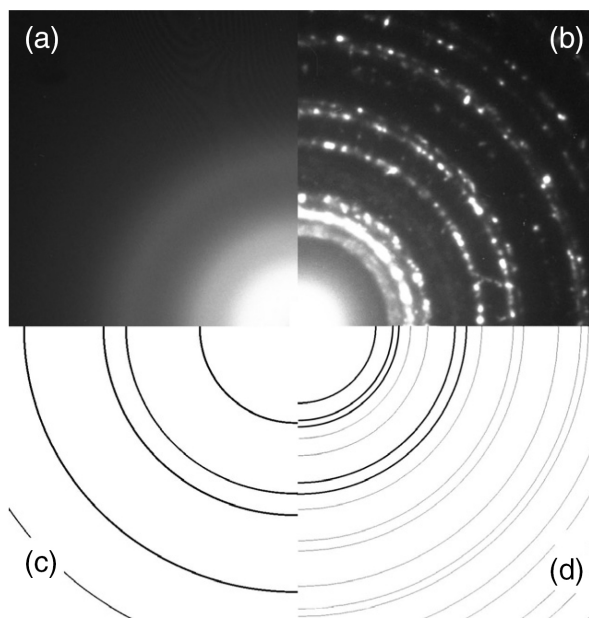


Figure 5. Selected area transmission electron diffraction pattern of boron carbide film, formed by PECVD and detached from its Si substrate then transferred to a Cu grid: (a) unprocessed, and (b) bombarded by 5.4 keV Ar ions, with (c) and (d) the corresponding fits to the rings in (a) and (b). Cu transfer by the Ar ions resulted in some additional rings in (d).

peating units, but do give rise to coherent elastic electron scattering (diffraction) from regions at least 10 nm in size in the case of Figure 5(b).

The much smaller size of crystals found in as-deposited boron carbide results in the diffuse rings of the corresponding pattern in Figure 5(a). The distances of the diffraction spots or rings from the center of such patterns correspond to the interplanar spacings within each crystal. While there is close agreement with interplanar spacings in known boron-carbon polytypes and between the fitted radii of boron carbide rings (Figures 5(c) and (d)) [23], these diffraction data do not match completely with known polytypes [5–11]. We cannot at this point directly relate the different structural polytypes of the C_2B_{10} boron carbides with the those polytypes identified by electronic structure. Electron and x-ray diffraction identification of exact crystal structures is a challenging problem given that carbon and boron have adjacent atomic numbers and low Z values. The structures of the two most well known boron carbide polytypes, based on the icosahedron, contain both direct and bridged links between adjacent icosahedra [6–8, 10]. The possible existence of such bridging links adds a number of opportunities for different carbon atom placement in the lattice, though these bridging links are not compellingly evident in our data. Modeling studies [9, 11] are insufficiently advanced to completely take into account the statistical (or non-statistical) variation of atomic identity within the solid state. Nonetheless, it has been experimentally shown that at least for $B_{11+n}C_n$ ($n = 1-3$) there is significant variation in the location and number of carbon atoms depending on the method of production. Given the difficulties in obtaining the exact physical structure of the various boron carbides,

spectroscopies can be used to identify differences in polytype, as indicated in this work.

It is clear that the nominally C_2B_{10} boron carbides comes in several polytypes, much like silicon carbide (a material well known for multiple polytypes). Generally these different polytypes have been associated with changing composition such as increasing the boron concentration [3, 4, 6, 10, 24–34] or replacing carbon with other main group elements such as phosphorus [35, 36], aluminum [37–41] and other main group elements.

We have identified different polytypes of the semiconducting boron carbides with large direct band gaps (materials formed from *para*-carborane and dimeric phosphorus bridged *ortho*-carborane ($C_2B_{10}H_{10}PCl_2$) and those with smaller band gaps (materials formed from *ortho*-carborane and *meta*-carborane). All of these materials have the same nominal boron to carbon ratio (C_2B_{10}). Furthermore, the materials can be either p-type (materials formed from *ortho*-carborane) or n-type (materials formed from *meta*-carborane) without the necessity of transition metal doping [13, 14]. All the boron carbide samples studied here are based upon C_2B_{10} , so that impurities cannot completely be used to explain the differences in polytype except in the case of phosphorus. It may well be (and this does seem the likely explanation) that phosphorus, even small amount, stabilizes a wider band gap boron carbide material.

What remains to be addressed is how the differing nature of the electronically different semiconducting boron carbides, as determined by optical properties and electrical characterization, is related to their solid state structures. This matter continues to be unresolved in spite of decades of effort [1–5, 9, 11]. Establishing this relationship between electronic structure and the different possible structural polytypes presents a great challenge because of the complexities inherent in a material in which the two constituents are essentially interchangeable [9, 11] and which use icosahedra as basic building blocks. The complexity is enhanced by the very small differences in scattering cross-section between boron and carbon [6–8, 10] and it is clear that a great deal of ingenuity will be required to solve this problem.

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