

Novel semiconducting alloy polymers formed from *ortho*-carborane and 1,4-diaminobenzene

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ABSTRACT

Novel semiconducting polymers have been formed via the electron-induced cross-linking of *ortho*-carborane ($B_{10}C_2H_{12}$) and 1,4-diaminobenzene. The films were formed by co-condensation of the molecular precursors and 200 eV electron-induced cross-linking under ultra-high vacuum (UHV) conditions. Ultraviolet photoemission spectra show that the compound films display a shift of the valence band maximum from ~ 4.3 eV below the Fermi level for pure boron carbide to ~ 1.7 eV below the Fermi level when diaminobenzene is added. The surface photovoltage effect decreases with decreasing B/N atomic ratio. Core level photoelectron spectra indicate site-specific bonding between B sites non-adjacent to icosahedral carbon sites on the carborane moiety, and carbon sites on the diaminobenzene moiety. Molecular orbital calculations and experiment suggest significant electronic interaction between *ortho*-carborane and 1,4-diaminobenzene units, with the highest occupied valence band states predominantly 1,4-diaminobenzene in character.

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1. Introduction

Materials based on carborane icosahedra ($B_{10}C_2H_{12}$) [1] are of broad interest in such areas as the fabrication of semiconducting boron carbides ($B_{10}C_2H_x$) [2–4], hydrogen absorption and storage [5], novel molecular architectures [5–9], all-boron carbide neutron detectors [10–17], biomedical applications [18], and recently, spintronics [19] and molecular electronics [20]. In many of these applications, the ability to systematically vary the valence electronic structure and properties of the material by doping [21–26] or incorporation of other molecular species [27] is of obvious interest.

We report here on the altered electronic properties of a novel polymer formed by electron beam induced cross-linking of *ortho*-carborane with 1,4-diaminobenzene (DAB). $B_{10}C_2H_{12}$ molecular films are wide band gap semiconductors due to the large highest occupied to lowest unoccupied molecular orbital gap [28–32] and the high ionization potential of carboranes [32,33]. Dehydrogenation during cross-linking of the carborane units closes the band gap significantly to form an indirect band gap of about 0.7–0.9 eV [23,34–37]; although this remains controversial in spite of optical measurements of the gap [34]. Recently, reported valence band photoemission results for self-assembled monolayers of

carborane/thiol hybrids on Au(111) indicate that this does little to alter the band gap, resulting in a valence band maximum ~ 4.3 eV below the Fermi level [20], similar to results for pure $B_{10}C_2H_x$ films derived entirely from *ortho*-carborane precursors [4]. In contrast, alloyed and cross-linked boron carbide/DAB films formed in our experiments (B/N ratio atomic ratio ~ 4 – 4.9) exhibit a valence band maximum at 1.7 eV below the Fermi level. Additionally, the results reported here indicate that the bonding between *ortho*-carborane icosahedra and DAB involve bonds between the DAB carbon sites and carborane boron sites bound only to other borons (B–B–H sites) as opposed to C–B–H or C–H sites on the icosahedra. The resulting electronic properties are indicative of a true alloyed material, rather than the sum of non-interacting *ortho*-carborane and DAB moieties.

2. Experimental methods

Experiments were carried out in a UHV system that has been described previously [38]. Briefly, the system had a base pressure of 3×10^{-10} Torr, and was equipped with a 140 mm mean radius hemispherical analyzer and channel plate detector. XPS spectra were acquired with a commercially available unmonochromatic $Al_{K\alpha}$ X-ray source. UPS spectra were acquired with a commercial, differentially pumped discharge source, using He I excitation (21.2 eV). XPS and UPS spectra were acquired in the constant pass energy mode with pass energies of 23.5 eV and 2.95 eV,

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respectively. The system was also equipped with an Ar ion sputter gun and commercial electron gun for e-beam induced cross-linking. The sample manipulator allowed for sample heating or cooling between 1000 K and 110 K by a combination of resistive heating and liquid N₂ cooling. Sample temperature was monitored with a type K thermocouple in proximity to the sample.

Ortho-carborane and 1,4-diaminobenzene (spectral grade) were obtained from commercial sources, then purified by freeze–pump–thaw procedures and admitted into the UHV chamber via separate manual leak valves. For *ortho*-carborane and 1,4-diaminobenzene sublimation into UHV, the precursor glass containers, stainless steel gas lines, and manual leak valves were heated to ~330 K and ~350 K, respectively. Pressures in the chamber were monitored using a nude ion gauge out of the line of site to the sample. *Ortho*-carborane and 1,4-diaminobenzene (DAB) exposures are reported here in terms of Langmuir (*L*) (1 *L* = 10⁻⁶ Torr s) and have not been corrected for ion gauge sensitivity or flux to the sample surface.

Films were formed by condensing precursors onto a 1 × 1 cm² copper foil cooled to 110 K under UHV conditions. Cross-linking was carried out by a 200 eV electron beam using the electron gun set to a constant emission current. This approach has proven effective in similar experiments [23]. Electron flux to the surface was not measured directly. XPS and UPS spectra were acquired before/after cross-linking at 110 K and after subsequent warm up to 300 K.

Spectra were referenced to a Cu (2p_{3/2}) binding energy of 932.7 eV [39]. The thicknesses of the deposited films (*d*) were estimated according to:

$$I = I_0 \exp\left(\frac{-d}{\lambda}\right) \quad (1)$$

where λ is the calculated [40] inelastic mean free path of 14.88 Å for a Cu (2p_{3/2}) electron through a B₁₀C₂H_x film. Relative atomic concentrations were determined according to [39,41]:

$$\frac{N_x}{N_y} = \left(\frac{I_x}{I_y}\right) \left(\frac{A_y}{A_x}\right) \quad (2)$$

where N_x and N_y are the atomic concentrations of species *x* and *y*; I_x , I_y are corresponding integrated core level peak intensities, and A_x , A_y are the corresponding atomic sensitivity factors (corrections that include the analyzer transmission function) appropriate to this analyzer [39]. The use of absolute, rather than relative experimental intensities in (1) and (2) introduces some potential error due to slight fluctuations in X-ray flux and sample position, but experience with this analyzer indicates that such error may be conservatively estimated at <10%.

2.1. The theoretical approaches

The orbital energies of the single molecules were calculated using both the semiempirical (PM3) and the hybrid density function theory (DFT B3LYP) methods, as has been undertaken successfully elsewhere [32,42–49]. Geometric optimization of the system was performed by obtaining the lowest unrestricted Hartree–Fock (UHF) energy states. DFT calculations were done with the Spartan package 06, with the standard 6-31G* basis set. A model density of states was obtained by applying equal Gaussian envelopes of 1 eV width to each molecular orbital at the ground state binding energies to account for the solid state broadening in photoemission and then summing together with a rigid energy shift of a typical value of 5 eV and 2.7 eV applied to the calculated electronic structure by PM3 and DFT, respectively. In the case of the semiempirical calculation, much of this shift takes into account the work function. We expect a number of differences between experiment and theory, since both methods calculate the ground state

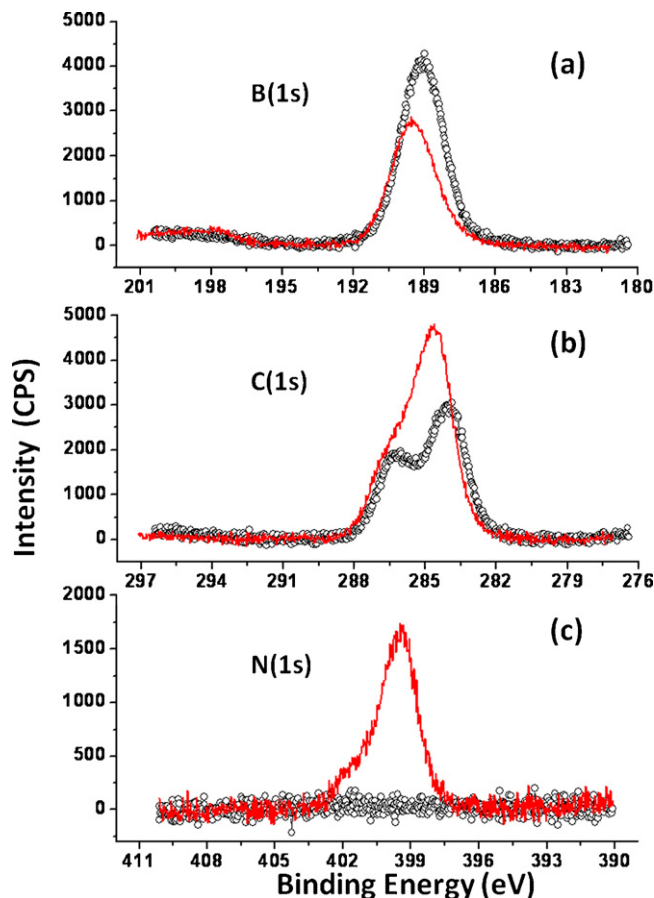


Fig. 1. (a) B(1s), (b) C(1s) and (c) N(1s) core level spectra for a 90 Å thick pure boron carbide film (open circles), and a 90 Å thick boron carbide/DAB film (solid red line) with a B/N atomic ratio of 4.9. Spectra acquired at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

electron structure, while photoemission and inverse photoemission are final state spectroscopies. Further, these are single molecule calculations, and the molecules studied here are screened in the final state by substrate and matrix ensemble. No corrections were made for photoemission matrix element effects.

3. Results

3.1. Core and valence band spectra

B(1s), C(1s), and N(1s) spectra acquired at room temperature are displayed in Fig. 1 for a film composed solely of cross-linked *ortho*-carborane (open circles), and an *ortho*-carborane/DAB film (solid red line). Both films have an estimated film thickness of 90 Å, and the *ortho*-carborane/DAB compound film has a B/N ratio of 4.9, indicating equal concentrations of *ortho*-carborane and DAB moieties in the film. Small amounts of O(1s) intensity (not shown) were observed for both pure *ortho*-carborane and the compound films. The total intensities were small and variable from experiment to experiment, indicating that the oxygen was most likely due to incidental OH/O condensation and incorporation during cross-linking at low temperature.

The B(1s) and C(1s) spectra for the pure carborane film (Fig. 1a and b) are typical of those observed for B₁₀C₂H_x films [3,50–52] as well as condensed *ortho*-carborane multilayers [53]. The B(1s) peak maximum is near 189 eV and is composed of bonding environments due to B–B–H species and C–B–H species (at a higher

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