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Significant magneto-resistive effects in boron carbide thin films

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ABSTRACT

We have found large room temperature magneto-resistance in boron carbides fabricated via electron-induced cross-linking of icosahedral *closo*-1,2-dicarbadodecaborane (*ortho*-carborane; 1,2-$B_{10}C_2H_{12}$) in the presence of the aromatic compound 1,4-diaminobenzene (DAB). X-ray photoemission spectroscopy confirms that the electron beam irradiation leads to site-specific cross-linking of the ortho-carborane, with cross-linking between B sites non-adjacent to icosahedral carbon sites on the carborane moiety, and carbon sites on the diaminobenzene moiety. The *I*–*V* curves, as a function of external magnetic field, demonstrate that significant room temperature negative magneto-resistance ($>50\%$) is possible in the resulting dielectric thin films. Inclusion of 1,4-diaminobenzene (DAB) is not essential for significant negative magneto-resistance, as crosslinking of *ortho*-carborane (1,2-$B_{10}C_2H_{12}$) results in large negative magneto-resistance, over 100%, depending on bias voltage.

1. Introduction

Boron carbide films have attracted considerable attention for applications such as neutron detection [1–4] but are also of interest as possible spintronic materials [5–7]. Materials without a transition metal or rare earth can exhibit significant magneto-resistance effects. Specifically, such effects are known [8–11] for graphene with a variety of defects. In the fluorinated graphenes [10,11], negative magneto-resistive effects are much diminished at room temperature, but such effects have also been observed [12,13] for boronated graphites (a boron carbide in fact), albeit at low temperatures (4 K). Semiconducting boron carbides tend to be both highly resistive [12–14] and very defective [15,16], so there may be considerable enhancements to be had in the magneto-resistance of a heterostructure containing some boron carbides. This work addresses whether large room temperature magneto-resistance effects are in fact possible in semiconducting boron carbides, formed by cross-linking [17–19] of the icosahedral *closo*-1,2-dicarbadodecaborane (*ortho*-carborane; 1,2-$B_{10}C_2H_{12}$) in the presence of 1,4-diaminobenzene (DAB)–BC:DAB films, or by cross-linking ortho-carborane without DAB additions (BC films).

2. Experimental

Boron carbide films were formed as described in prior work [17–20] by electron beam cross-linking of the component source molecules after condensation. The *ortho*-carborane and 1,4-diaminobenzene were obtained from commercial sources, then purified by freeze-pump-thaw procedures and admitted into the UHV chamber via separate manual leak valves. In the case of *ortho*-carborane, the precursor glass container, stainless steel gas line and manual leak valve were heated to ~330 K to enhance sublimation, and ~360 for diaminobenzene. Pressures in the chamber were monitored using a nude ion gauge out of line of site to the sample. Films were formed by condensation of *ortho*-carborane or co-condensation of *ortho*-carborane and an aromatic linking unit, 1,4-diaminobenzene (DAB), at ~120 K on silicon oxide substrates prepatterned with permalloy (about 20% iron and 80% nickel) contacts separated by 15 μm under UHV conditions. Cross-linking was carried out using a 200 eV electron beam using an electron gun. After the deposition and subsequent electron beam induced cross-linking, the films were allowed to warm to room temperature and later flash annealed to 600 K to remove any non-crosslinked diaminobenzene (DAB), in the case of boron carbide DAB containing films (BC:DAB).

X-ray photoemission spectroscopy (XPS) spectra were acquired with a 140 mm mean radius hemispherical analyzer with a channel plate detector, operated in constant pass energy mode (23.5 eV), with unmonochromatized Al Kα radiation. XPS spectra were calibrated by setting the Si 2p core level photoemission peak binding energy,

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in SiO_2, at 103.3 eV [21]. Based on relative core-level intensities, BC: DAB compound film exhibits a B/N atomic ratio of 3.2—compared to the nominal value of 5 for a 1:1 BC:DAB film,. The core level binding energies and intensities indicate that flash annealing the films from 300 K to 600 K in UHV has little effect on the local chemistry. Small amounts of O contamination were observed for both BC and BC:DAB films. The total O(1s) 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 magnetoresistance (MR) curves were obtained by fixing the applied bias, and running a sweep scan of the current across the film surface as a function of the applied external magnetic field on the thin films, which have an estimated film thickness of 90–200 Å. *I–V* curves were carried out using a Keithley 236 source and plotted as a function of the in-plane external magnetic field. Samples were placed in a simple cryogenic system, and a magnetometer was used to generate fields ranging from −1 T (T) up to +1 T (T). All transport measurements were carried out at room temperature.

3. Results and discussion

The measured X-ray photoemission binding energies are 189.5 eV, 284.7 eV and 399.3 eV for the B (1s), C (1s) and N (1s) core levels, respectively for the cross-linked BC:DAB films, as shown in Fig. 1. These values are in agreement with those obtained in B(1s), C(1s), and N(1s) spectra for films composed of ortho-carborane cross-linked with DAB [18]. The B(1s) and C(1s) core level photoemission spectra (Fig. 1a,b) are typical of those observed for $B_{10}C_2H_x$ films [17–20,22–24], as well as condensed ortho-carborane multilayers [25]. The B(1s) peak maximum is near 189 eV and is composed of bonding environments due to B–B–H species and (at a higher binding energy) C–B–H species [17–20,22]. The C(1s) core level photoemission spectrum (Fig. 1b) features two peaks characteristic of carbon atoms within the icosahedron and the carbon indicative of DAB [18,19]. The N(1s) core level photoemission spectra of the composite film (Fig. 1c) exhibits a peak maximum identical to that of condensed DAB film [18,19]. The lack of significant perturbation of the N(1s) core level photoemission spectra from that of condensed DAB indicates that the N sites are not perturbed by the cross-linking process. Cross-linking of ortho-carborane in the absence of DAB resulted in B(1s) and C(1s) binding energies and intensities (not shown) in excellent agreement with previous results [20]. Therefore, the core level spectra indicate that cross-linking of ortho-carborane and DAB results in a film composed of carborane icosahedra bonded to intact DAB species predominantly via B–B–H sites on the icosahedra and the carbon sites on the DAB units. In the absence of DAB, crosslinking produces a BC film consisting of icosahedra produced by cross-linking at B sites non-adjacent to icosahedral carbon sites. These results are in accord with recently reported results [17–20].

The room temperature negative magneto-resistance for the BC: DAB films is illustrated in Fig. 2. The high resistivities are characteristic of the plasma enhanced chemical vapor deposition of semiconducting boron carbides [14] where a resistance of 10^{10} Ω-cm is typical. For samples with a fixed bias voltage of 20 V, the magneto-resistance decreased by about 16%, a much

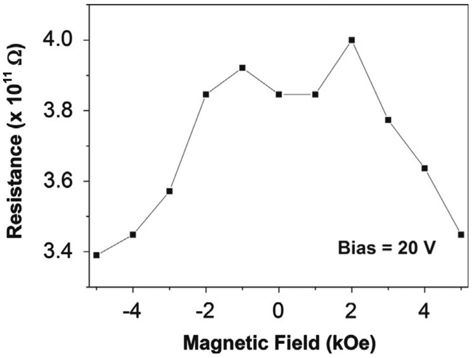

Fig. 2. Magnetoresistance for a BC-DAB film at room temperature at a 20 V bias. The distance between contacts is about 15 μm.

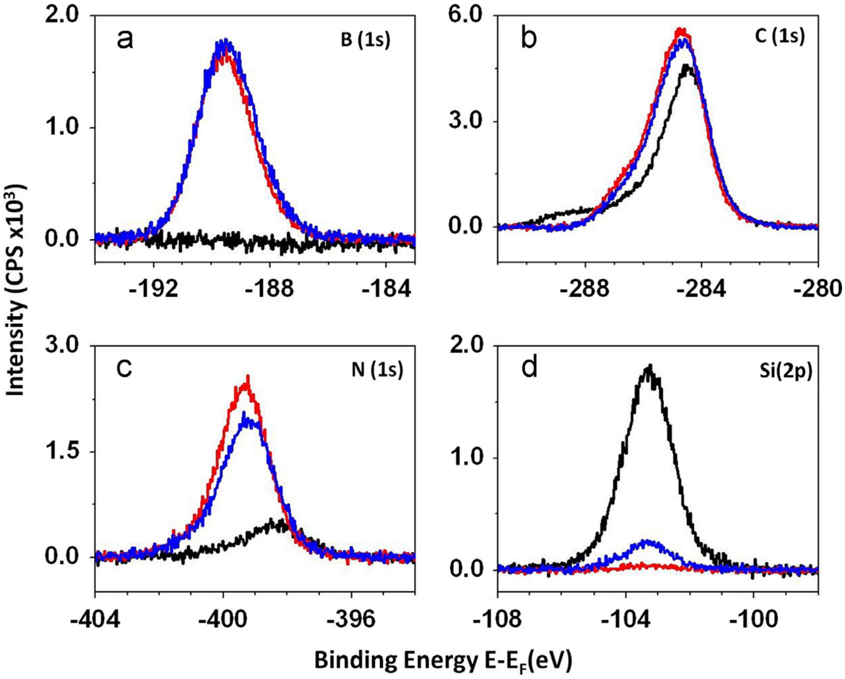

Fig. 1. Shows the core level spectrum of the (a) B(1s), (b) C(1s), (c) N(1s) and (d) Si(2p) for BC-DAB films. The black trace represents silicon oxide substrate prepatterned with permalloy at a temperature of approximately 120 K, the red trace correspond to the films after warmed to room temperature and the blue trace represents after flash annealed to 600 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)