

**Novel cross-linked  $B_{10}C_2H_x$  and  $B_{10}C_2H_x:Y$  ( $Y=1,4$ -diaminobenzene, pyridine, benzene) films: anomalously large room temperature magnetoresistance and tunable electronic structure in a new class of boron carbide-based polymer.**

Frank L. Pasquale<sup>1</sup>, Robinson James<sup>1</sup>, Raymond Welch<sup>1</sup>, Elena Echeverria<sup>2</sup>, P. A. Dowben<sup>2</sup>, and J. A. Kelber<sup>1\*</sup>

<sup>1</sup>Department of Chemistry and Center for Electronic Materials Processing and Integration, 1155 Union Circle #305070, University of North Texas, Denton, TX 76203, USA

<sup>2</sup>Department of Physics and Astronomy, Nebraska Center for Nanostructures and Materials, 855 North 16<sup>th</sup> Street, Theodore Jorgensen Hall, University of Nebraska-Lincoln, Lincoln, NB 68588-0299, USA

A new class of semi-conducting boron carbide polymeric materials has been formed from the cross-linking of ortho-carborane ( $B_{10}C_2H_{12}$ ) and  $B_{10}C_2H_{12}$  in the presence of aromatic compounds (1,4-diaminobenzene, pyridine, and benzene) to form  $B_{10}C_2H_x$  and  $B_{10}C_2H_x:Y$ , respectively. Core and valence band photoemission studies, indicate that cross-linking of  $B_{10}C_2H_{12}$  results in site-specific bonding between boron sites opposite carbon sites on the carborane icosahedra. This site specific cross-linking is retained when cross-linking  $B_{10}C_2H_{12}$  in the presence of aromatic linking units, with the linking units inserting themselves between carborane icosahedra. This insertion results in bonding between boron sites opposite carbon sites in the carborane icosahedra to carbon sites on the aromatic moieties. These  $B_{10}C_2H_x:Y$  films exhibit shifts in the valence band maximum from -3.9 eV (i.e. 3.9 eV below the Fermi level) for  $B_{10}C_2H_x$ , to -2.2 eV, -1.7 eV and -1.3 eV for  $Y =$  benzene, pyridine, or 1,4-diaminobenzene, respectively. In all cases, the states near the top of valence band correspond to states localized on the linking unit. Surprisingly, these materials exhibit anomalously large (> 50%) positive and negative magnetoresistance at room temperature, where conductivity ( $C$ ) decreases (or increases) in the presence of an applied magnetic field ( $H$ ):  $MR = [C_H - C_0]/C_0$ . The sign and magnitude of the magnetoresistance are dependent on film composition and method of synthesis. A variety of boron carbide dopants have been modeled suggesting that control of the sign and magnitude of the magnetoresistance may well be possible over a wide dynamic range and for a wide variety of heterostructures. The ability to tune electronic and magnetoelectric properties in these materials suggests multiple applications in radiation sensing, nanoelectronics, and spintronics.

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