The local structure of transition metal doped semiconducting boron carbides

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Abstract
Transition metal doped boron carbides produced by plasma enhanced chemical vapour deposition of orthocarborane (closo-1,2-C2B10H12) and 3d metal metallocenes were investigated by performing K-edge extended x-ray absorption fine structure and x-ray absorption near edge structure measurements. The 3d transition metal atom occupies one of the icosahedral boron or carbon atomic sites within the icosahedral cage. Good agreement was obtained between experiment and models for Mn, Fe and Co doping, based on the model structures of two adjoined vertex sharing carborane cages, each containing a transition metal. The local spin configurations of all the 3d transition metal doped boron carbides, Ti through Cu, are compared using cluster and/or icosahedral chain calculations, where the latter have periodic boundary conditions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Although transition metal doping of β-rhombohedral boron has been heavily investigated [1–5], the doping of semiconducting boron carbides has been driven largely by device applications. The ability to generate semiconducting grades of boron carbide by plasma enhanced chemical vapour deposition (PECVD) of carboranes permits the development of corrosion resistant, high temperature devices with many applications including neutron detection [6–14]. This PECVD based semiconducting boron carbide has been used to fabricate heterojunction diodes with silicon [6–10, 15, 16], silicon carbide [17] and other semiconducting boron carbides (making these devices all boron carbide devices) [11, 13, 14, 18] and a boron carbide transistor [19]. Boron carbide homojunctions have been fabricated by PECVD of carboranes, with nickel doping [20, 21], cobalt doping [22] and iron doping [23], as indicated in figure 1. Indeed, nickel doping of boron carbide has opened a route to the fabrication of the first boron carbide Esaki tunnel diode [20, 21].

Successful n-type doping of β-rhombohedral boron has been accomplished with dopants such as iron [1–4], vanadium [4], chromium [4], nickel [4] and cobalt [4], while Cu is a p-type dopant [5]. For the related boron carbides, nickel [20, 21, 24, 25] and iron [23] are certainly n-type dopants while cobalt may or may not [22] be a p-type dopant of the boron carbides, depending upon device temperature. The common route for semiconducting doping is to include a metallocene, M(C5H5)2, M = V, Cr, Mn, Fe, Co, Ni, simultaneously with the carborane source molecule, during PECVD [20–25]. This chemistry provides a significant range of possible 3d transition metal dopants of boron carbide, but a unified picture of the possible differences (and similarities) in local structure and electronic structure adopted
Figure 1. The I–V characteristics of (a) Ni(n)-B_{10}C_{2}/(p)-B_{10}C_{2} [20], (b) Co(n)-B_{10}C_{2}/(p)-B_{10}C_{2} [22] and (c) Fe(n)-B_{10}C_{2}/(p)-B_{10}C_{2} [23] diodes, formed by the PECVD decomposition of orthocarborane and the appropriate metallocene (see text). The insets are schematics of the various diodes, as assembled.
excitation) is roughly:
\[
\chi(k) = k^{-1} f(k, \theta) \sum_i W_i \sin[2kR_i + \alpha(k)]
\times \exp(-\gamma R_i - 2\sigma_i^2 k^2),
\]
where \( f(k, \theta) \) is the atomic scattering factor and the weight from the atoms in each shell radius \( i \), from the metal atom, is given in terms \( W_i \). A typical experimental \( \chi(k) \) spectrum weighted by \( k \) demonstrates good data quality up to \( \sim 11\,\text{Å}^{-1} \).

3. The local structure in the vicinity of the transition metal dopant

We have performed Fe and Mn K-edge XANES and EXAFS measurements of Mn and Fe doped PECVD grown semiconducting boron carbides ‘\( \text{C}_2\text{B}_{10}\text{H}_{12} \)’. The normalized Mn K-edge XANES spectrum of Mn-doped boron carbide, and the Fe K-edge XANES spectrum of Fe-doped boron carbide are shown in figure 2.

The characteristic signatures of manganese and iron are evident at values close to the expected [33] Mn K-edge (\( E_F - E_K \) at 6539 eV (figure 2(a)) and Fe K-edge (\( E_F - E_K \) at 7112 eV (figure 2(b)), respectively. We can infer from figure 2 that manganocene and ferrocene source gases do result in manganese and iron doping, respectively, of the PECVD grown boron carbides. This establishes that the sublimed molecular vapours of the various metallocenes (\( M(\text{C}_5\text{H}_5)_2 \), \( M = \text{Fe} [23], \text{Co} [22, 26] \) or \( \text{Mn}, \) ), when added to the other PECVD source gases, appear to behave in a similar fashion in delivering the transition metal dopant during the plasma CVD process, although the similarities are in fact more significant as discussed below.

There are some distinctive features at the absorption edge of the Fe-doped boron carbide, indicating strong hybridization between iron and the inorganic host matrix. This is similar, in some respects, to that observed for the Co-doped PECVD grown ‘\( \text{C}_2\text{B}_{10}\text{H}_{12} \)’ semiconducting boron carbides, using cobaltocene [22–26]. The K-edge absorption is perhaps strongest for the Mn-doped boron carbide (as compared with the Fe [23] or Co [22, 26] doped semiconducting PECVD boron carbide).

The Fourier transformed EXAFS wave vector weighted \( k\chi(k) \) data, in radial coordinates, were obtained for Mn (solid lines in figure 3) and Fe (figure 4(b)). The radial positions of peaks represent the distance between the absorbing Mn or Fe atom and their near neighbours within 6 Å. This makes possible acquisition of some structural and geometrical information of Mn or Fe doped boron carbides at a local level. The amplitude gives a qualitative description of the number of neighbours, and provides an overall sense of the local order. It is fairly clear from visual inspection of the magnitudes of the Fourier transformed EXAFS wave vector weighted \( k\chi(k) \) data that the local order about the Mn (figure 3) or Fe (figure 4(b)) transition metal atoms in semiconducting boron carbide is far greater than previously observed for cobalt doping of PECVD semiconducting boron carbide (figure 4(a)) [22, 26]. In the case of the latter, the nearest neighbour and next nearest neighbour shells about the transition metal have strong components, but weaken dramatically with increasing radius compared with Fe, and particularly Mn-doped semiconducting boron carbides.

The major peak in the Fourier transformed EXAFS \( k\chi(k) \) data at 1.4 Å is due to single-scattering contribution of Mn–B(C) (figure 3) or Fe–B(C) (figure 4(b)) pairs, which can be considered as nearest neighbours with the pertinent transition metal dopant. Peaks observed between 1.96 and 4.5 Å are due to \( M–X \) pairs (where \( M = \text{Mn} \) in figure 3 and Fe in figure 4(b), while \( X \) could be either boron or carbon) and multiple scattering contributions, as occurs with increasing radius from the transition metal. The peak at 4 Å in the Fourier transformed EXAFS \( k\chi(k) \) data corresponds to other Mn–B(C) (figure 3) or Fe–B(C) (figure 4(b)) pairs with longer distance from the Mn or Fe atom. The feature at about 5 Å is associated with the \( M–M \) pairs.

Figure 2. Normalized Mn (a) and Fe (b) K-edge XANES spectra of Mn and Fe doped PECVD semiconducting boron carbides, respectively. The Mn K-edge energy (\( E_F - E_K \) at 6539 eV (a)) and Fe K-edge energy (\( E_F - E_K \) at 7112 eV (b)) are highlighted, where \( E_K \) is the K-edge energy adapted from [33].
Figure 3. The Fourier transformed EXAFS $k\chi(k)$ data for the manganese doped PECVD semiconducting boron carbide are compared with the theoretical Fourier transformed EXAFS $k\chi(k)$ (broken line), using the schematic model of figure 5. The data are transformed for data taken between 4 and 8 Å.

EXAFS using the FEFF-6 codes. Geometry optimization was performed for a number of possible structural models by obtaining the lowest unrestricted Hartree–Fock energy states. Similar to the prior studies with cobalt doping of semiconducting boron carbides [22, 26], a number of local structural cluster models were tested for fit to the experimental EXAFS data.

Among the tested models, the best fit of the unfiltered EXAFS data is from the model of two adjoined icosahedral cages with Mn or Fe atom sitting in the apical icosahedral sites, possibly at a boron or carbon site for each cage, as schematically shown in figure 5. The separation between two paired Fe ions is about 5.03 ± 0.03 Å while the Mn–Mn separation was found to be close to 5.15 ± 0.03 Å, all similar to the values found for Co–Co pairs in cobalt doped boron carbide where the $M$–$M$ separation was found to be about 5.28 ± 0.02 Å. We find that this model (figure 5), involving transition metal atom $M$–$M$ pairs sitting in the apical sites on opposite sides of the adjacent icosahedra, reasonably accounts for all major features shown in the EXAFS spectra for all three transition metal doped PECVD semiconducting boron carbides. The difference in magnitudes between the experimental and modelling curves mainly reflects low concentration of manganese or iron in the material. Other tested models, in which the metal atoms are not paired, do not show agreement with the experimental data, especially in the region corresponding to lattice constants greater than 3 Å. This effect was noted previously in the studies of cobalt doped boron carbides [22, 26]. Compared with the case of cobalt doped boron carbides, the modelling of the EXAFS data favours the formation of metal–metal pairs to an even greater extent with Mn and Fe doping, but in all cases the peak locations for Mn–Mn, Fe–Fe and Co–Co pairs are all very close, at about 5 Å.

The distance for the single-scattering contributions from both the Mn–B(C) nearest neighbour pairs and Fe–B(C) pairs is about 1.4 Å, smaller than for the cobalt case (1.8 Å). This suggests that the manganese and iron atoms prefer to sit in the icosahedral apical sites in positions much closer to the boron and carbon atoms than is the case for cobalt. This tends to
Figure 6. The spin distribution on the optimized structure, with an isovalue of 0.0179 a.u for the stable ferromagnetic high spin (a), (c) and less stable low spin (b), (d) configurations of Fe pairs on opposite sides (UD) of the adjacent icosahedra for both the infinite chains structures with periodic boundary conditions, i.e. Fe$_2$–C$_2$B$_{20}$H$_{14}$ (as shown in (a) and (b)) and the clusters Fe$_2$–C$_2$B$_{20}$H$_{18}$ (as shown in (c) and (d)).

indicate the greater stability of the Mn and Fe doped boron carbide structures and stronger bonds formed between B(C) and either Mn or Fe atoms.

The \textit{ab initio} Co K-edge XANES \cite{22, 26} and Co, Fe and Mn EXAFS spectra simulations suggest that all three transition metals adopt an endohedral position occupying apical sites within the icosahedral cage, as indicated in figures 5 and 6, giving the transition atom a five-fold coordination to the \textit{nido}-carborane CB$_{11}$ cage. This is very much like a number of known metalloboranes \cite{34}. In some of the known metalloborane examples, there is a conversion of adjacent icosahedra by removal of a B, BH, C or CH vertex, followed by introduction of the (C$_5$H$_5$)M vertex \cite{34, 35}. This should be a facile reaction \cite{34}. Given the structural similarities among all three transition metal doped semiconducting PECVD boron carbides, we can make now some estimates of electronic structure, at least in the region of the transition metal dopant, from \textit{ab initio} theory. Two approaches are possible: cluster calculations using M$_2$–C$_2$B$_{20}$H$_{18}$ clusters (M = Ti, V, Cr, Mn, Fe, Co, Ni and Cu), as were used to help solve and fit the EXAFS data, or chains of doped icosahedra with periodic boundary conditions.

4. The local electronic structure and likely local spin configurations for the transition metal doped semiconducting boron carbides

All the first-principles calculations are performed in the framework of density functional theory as implemented in the DMol$^3$ code \cite{36, 37}. The PW91 generalized gradient approximation (GGA) was used for the exchange-correlation functional because of the better performance of GGA than the local density approximation (LDA) in many molecular systems. All the electrons were considered equally, and the double numerical plus polarization (DNP) basis set, which is comparable to the 6-31G** basis set, was used.
and Fe) and the clusters \( M_{2–C_2B_20H_{18}} \) with periodic boundary conditions, i.e. \( M_{2–C_2B_20H_{18}} (M = Ti, V, Mn, Mn, Fe, Co, Ni and Cu) \), as shown in figure 6, with the latter numbers in brackets ( ). The total energy difference (eV) between the high- and low-spin configurations and average magnetic moment magnitude (\( \mu_B \)) per atom with the metal pairs on the opposite sides of the adjacent icosahedra for both the clusters \( M_{2–C_2B_20H_{18}} \) with periodic boundary conditions, i.e. \( M_{2–C_2B_20H_{18}} (M = Ti, V, Mn, Mn, Fe, Co, Ni and Cu) \), molecular clusters have also been tabulated with the latter numbers again in brackets ( ).

<table>
<thead>
<tr>
<th>Metal</th>
<th>( E_{uu} - E_{ud} ) (eV)</th>
<th>( E_{high - spin} - E_{low - spin} ) (eV)</th>
<th>Average magnetic momentum (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.46 (0.32)</td>
<td>-0.002 (0.00)</td>
<td>0.85 (1.05)</td>
</tr>
<tr>
<td>V</td>
<td>0.59 (0.34)</td>
<td>-0.02 (0.02)</td>
<td>2.15 (2.2)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.78 (0.51)</td>
<td>0.003 (0.13)</td>
<td>3.45 (3.2)</td>
</tr>
<tr>
<td>Fe</td>
<td>1.1 (0.44)</td>
<td>-0.24 (0.01)</td>
<td>1.1 (1.1)</td>
</tr>
<tr>
<td>Cr</td>
<td>(0.36)</td>
<td>(-0.03)</td>
<td>(3.5)</td>
</tr>
<tr>
<td>Co</td>
<td>(0.59)</td>
<td>Non-magnetic</td>
<td>Non-magnetic</td>
</tr>
<tr>
<td>Ni</td>
<td>(0.51)</td>
<td>Non-magnetic spin configuration</td>
<td>Non-magnetic spin configuration</td>
</tr>
<tr>
<td>Cu</td>
<td>(0.08)</td>
<td>Non-magnetic spin configuration</td>
<td>Non-magnetic spin configuration</td>
</tr>
</tbody>
</table>

Convergence tolerance for the self-consistent field is \( 2 \times 10^{-6} \) eV, and the structures were optimized till the maximum force is below 0.054 eV Å\(^{-1}\). To explore the possible magnetic ordering configurations, different initial spin states of the transition metal atoms in the spin-polarized calculated model systems were considered and optimized. Where possible, the electronic structure and spin configuration for metal atom pairs on the same (UU) and opposite sides (UD) of the adjacent icosahedra for both the infinite chain structures with periodic boundary conditions, i.e. \( M_{2–C_2B_20H_{18}} (M = Ti, V, Mn, Mn, Fe, Co, Ni and Cu) \), were analysed by using the Hirshfeld method (as implemented in DMol3), which has been shown to give chemically meaningful results [39]. The detailed average electron charges for the metal pairs on opposite sides of the adjacent icosahedra for both the infinite chain structures with periodic boundary conditions, i.e. \( M_{2–C_2B_20H_{18}} (M = Ti, V, Cr, Mn, Mn, Fe, Co, Ni and Cu) \), are summarized in table 2. The calculated average atomic charges differ little between the high- and low-spin configurations as calculated by the Hirshfeld method [39]. For comparison, the results by using the Mulliken method are also listed. Generally, the average charge state on each transition metal is in the range of 0.3–0.6 |e|, which suggests that the transition metal generally adopts a covalently bonded like scenario.

The bond lengths of the five \( M–B \) bonds are different for different spin configurations. There are small differences \( \delta L \) in the \( M–B \) bond lengths between the high- and low-spin configurations for Ti, V, Cr, Mn and Fe, as listed in table 3. While these bond length differences \( \delta L \) are small for some transition metal systems, there are differences nonetheless. We find a strong connection between the stable structures and the bond lengths that do depend upon the local spin configuration for Mn-doped clusters and chains. The bond length differences between the transition metal atoms and nearby boron atoms in the high- and low-spin ground states are very similar for all cases, with the maximum \( \delta L \) ranging at most from 0.004 to 0.009 Å, for Ti, V, Cr and Fe. However, in the case of Mn, \( \delta L \) is as large as 0.123 Å. In the non-magnetic systems containing Co, Ni and Cu, only an average bond length can be cited. Accordingly, we may expect slightly different fits to the experimental structural data from EXAFS for Ti, V, Cr, Mn and Fe doped PECVD semiconducting boron carbides, depending on the model spin configuration used, as indicated in figure 7.

Of course, for the PECVD grown semiconducting boron carbides, the transition metal atoms are very likely to be more highly coordinated than in the models of figure 6. We can expect that the greater coordination that is likely to occur in the semiconducting solid material will also result in changes to bond length as well as diminish any differences in the bond lengths between the high-spin and low-spin configurations. Generally, the \( M–B(C) \) bond lengths obtained from theory are in the region of 2 Å, as expected from the analysis of the EXAFS experiments, although somewhat larger as summarized in table 3. Again, this is expected for a metal atom that might not be as fully coordinated as may occur in the solid boron carbide semiconductor.

### 5. Conclusion

From the analysis of Mn and Fe K-edge XANES and EXAFS spectra, there are indications that the manganese and iron atoms are chemically bonded within icosahedral boron carbide cages of PECVD grown semiconducting boron carbides, in a
Table 2. The average atomic charges for the metal pairs on opposite sides of the adjacent icosahedra for both the clusters \(M_2-C_2B_{20}H_{18}\) (\(M = \text{Ti, V, Cr, Mn, Fe, Co, Ni and Cu}\)) and infinite chain structures with periodic boundary conditions, i.e. \(M_2-C_2B_{20}H_{14}\) (\(M = \text{Ti, V, Cr, Mn, Fe, Co, Ni and Cu}\)), as shown in figure 6. The average atomic charges calculated differ little between the high- and low-spin configurations as calculated by the Hirshfeld method [39] and again by the Mulliken method, shown in brackets ( ).

<table>
<thead>
<tr>
<th>Transition Metal</th>
<th>Atomic charge ((e^-/)) of the high-spin state</th>
<th>Atomic charge ((e^-/)) of the low-spin state</th>
<th>Atomic charge ((e^-/)) of the high-spin state</th>
<th>Atomic charge ((e^-/)) of the low-spin state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.652 (0.534)</td>
<td>0.652 (0.534)</td>
<td>0.617 (0.454)</td>
<td>0.617 (0.454)</td>
</tr>
<tr>
<td>V</td>
<td>0.559 (0.408)</td>
<td>0.561 (0.409)</td>
<td>0.541 (0.364)</td>
<td>0.541 (0.365)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.445 (0.241)</td>
<td>0.480 (0.271)</td>
<td>0.444 (0.251)</td>
<td>0.442 (0.243)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.388 (0.297)</td>
<td>0.389 (0.298)</td>
<td>0.379 (0.273)</td>
<td>0.386 (0.285)</td>
</tr>
<tr>
<td>Fe</td>
<td>0.291 (0.077)</td>
<td>0.318 (0.033)</td>
<td>0.281 (0.220)</td>
<td>0.281 (0.220)</td>
</tr>
<tr>
<td>Co</td>
<td>0.483 (0.109)</td>
<td>0.459 (0.018)</td>
<td>0.459 (0.018)</td>
<td>0.459 (0.018)</td>
</tr>
</tbody>
</table>

Table 3. The \(M-B\) bond and maximum length difference, \(\delta L\), between the high- and low-spin states of \(M_2-C_2B_{20}H_{18}\).

<table>
<thead>
<tr>
<th>(M)</th>
<th>High spin</th>
<th>Low spin</th>
<th>(\delta L) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2.184</td>
<td>2.181</td>
<td>0.003</td>
</tr>
<tr>
<td>V</td>
<td>2.152</td>
<td>2.156</td>
<td>−0.004</td>
</tr>
<tr>
<td>Cr</td>
<td>2.157</td>
<td>2.162</td>
<td>−0.005</td>
</tr>
<tr>
<td>Mn</td>
<td>2.087</td>
<td>2.210</td>
<td>−0.123</td>
</tr>
<tr>
<td>Fe</td>
<td>2.009</td>
<td>2.017</td>
<td>−0.008</td>
</tr>
<tr>
<td>Co</td>
<td>2.020</td>
<td>2.020</td>
<td>0</td>
</tr>
<tr>
<td>Ni</td>
<td>2.058</td>
<td>2.058</td>
<td>0</td>
</tr>
<tr>
<td>Cu</td>
<td>2.236</td>
<td>2.236</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 7. Comparison of the theoretical modelling of the Fourier transformed EXAFS of the iron doped PECVD semiconducting boron carbide. The magnitude of the Fourier transformed experimental EXAFS is shown as a solid line. The fitting curves are based on structural parameters calculated by semi-empirical calculation (dashed line) and density functional theory calculations with both the high-spin (dotted line) and low-spin (dash dot line) configurations, see text.

similar fashion to that observed for cobalt doping of PECVD grown semiconducting boron carbides. In all three transition metal examples for the doping of semiconducting boron carbides, the doping occurs pairwise with each transition metal sitting on adjacent adjoined icosahedral cages with a metal to metal spacing of about 5 Å. This observation is consistent with theory, while the adoption of an apical endohedral position within the cage, by the various transition metals, is consistent with known main group metalloborane synthetic chemistry [34, 35].

The spin density calculations indicate that Ti, V, Cr and Fe favour the high-spin stable ground states, while Mn prefers a low-spin antiferromagnetic configuration, and Co, Ni and Cu adopt local non-magnetic spin configurations.

Acknowledgments

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References


[34] Hawthorne M F 1968 Acc. Chemical Rev. 1 281


[37] Delley B 2000 J. Chem. Phys. 113 7756
