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NOVEL METHODS FOR DEPOSITION OF BORON CARBIDE FILMS

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ABSTRACT

By combining pentaborane (B₅H₉) and decarborane (B₁₀H₁₄) with methane in a plasma reactor, a variety of boron–carbides can be made over a wide range of compositions. The resulting thin films have uniform composition and appear to be polycrystalline.

INTRODUCTION

Boron carbides are of considerable interest because of their potential semiconductor properties [1,2] and because these materials are very hard, chemically inert and retain a high modulus of elasticity [3]. Boron carbides have applications as neutron absorbent materials [4–8], wear resistant hard coatings, and armor coatings [3,9,10]. There are a number of unusual boron containing films with hardness values comparable to diamond [9,10,11].

Until now boron carbides fabricated via chemical vapor deposition typically employ BCl₃ reacted with a hydrocarbon (typically methane) [12–16] though variations of this approach using BCl₃ + CCl₄ [17,18] or BBr₃ [19–21] have been employed. We have demonstrated that decarborane is a suitable boron source material for the fabrication of boron and boron nitride coating [22,23] and we now demonstrate that a wide range of boron carbide stochiometries can be fabricated by combining boranes and methane in an rf plasma reactor.

EXPERIMENTAL

Decarborane (14), B₁₀H₁₄, is an airstable white crystalline solid with a vapor pressure of several Torr at room temperature. The vapor pressure was increased for these experiments by heating (the vapor pressure at 100°C is 19 Torr), since the decarborane (14) decomposes only above 170°C [24]. The pentaborane (9), B₅H₉, with a vapor pressure of 209 Torr at 25°C, was a vapor under the operating conditions of our experiment.
The radio-frequency plasma deposition studies were carried out in a small 3-inch 13.56 mHz rf plasma reactor with a 1-inch plate separation. The typical rf power output of the reactor was 20W, but could be increased to 100W. The sample substrates (quartz glass or silicon) were mounted on the ground plate of the two plate system, with the other plate connected to the rf network. The system used a commercial rf generator and impedance matcher. Methane was used as the carbon source and no carrier gas was used.

Film composition was determined by Auger electron spectroscopy calibrated with B₄C after removing surface impurities resulting from exposure to air.

RESULTS

After setting up a stable gas mixture of the gaseous borane and methane the plasma was initiated and a film was deposited. The results for decaborane and pentaborane are summarized in tables one and two. Considering that the source gas contained no impurities, it is unsurprising that the pure films can be fabricated by this procedure as is indicated by the Auger electron spectra shown in figure one.

![Figure 1: Auger electron spectra of boron-carbide fabricated from 44\(\mu\) of CH₄ and 6\(\mu\) of B₂H₆ in a 20 watt rf plasma.](image)

Some oxygen incorporation was found upon exposing these films to air, particularly for the films fabricated from decaborane (14). In general the decaborane (14) films proved to be far less uniform. Decaborane (14) was far more difficult to control and vary the boron carbide film composition than pentaborane (9).
TABLE ONE: SUMMARY OF DEPOSITIONS USING B10H14 + CH4

<table>
<thead>
<tr>
<th>Ratio B10H14:CH4</th>
<th>B10H14 Press mTorr</th>
<th>CH4 Press mTorr</th>
<th>Temp °C</th>
<th>AES B%</th>
<th>AES C%</th>
<th>AES 0%</th>
<th>Thickness μm</th>
<th>Rate μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.75:1</td>
<td>4.75:1</td>
<td>9.5</td>
<td>2.0</td>
<td>396</td>
<td>&lt;10</td>
<td>50</td>
<td>50</td>
<td>–</td>
</tr>
<tr>
<td>5.25:1</td>
<td>21.0</td>
<td>4.0</td>
<td>398</td>
<td>15</td>
<td>25</td>
<td>60</td>
<td>0.120</td>
<td>0.0027</td>
</tr>
<tr>
<td>7.00:1</td>
<td>35.0</td>
<td>5.0</td>
<td>381</td>
<td>68</td>
<td>20</td>
<td>12</td>
<td>0.040</td>
<td>0.0012</td>
</tr>
<tr>
<td>7.00:1</td>
<td>42.0</td>
<td>6.0</td>
<td>368</td>
<td>82</td>
<td>12</td>
<td>6</td>
<td>0.119</td>
<td>0.007</td>
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TABLE TWO: SUMMARY OF DEPOSITIONS USING B5H5 + CH4

<table>
<thead>
<tr>
<th>Ratio B5H5:CH4</th>
<th>B5H5 Press mTorr</th>
<th>CH4 Press mTorr</th>
<th>Temp °C</th>
<th>AES B%</th>
<th>AES C%</th>
<th>AES 0%</th>
<th>Thickness μm</th>
<th>Rate μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td>5.0</td>
<td>45.0</td>
<td>449</td>
<td>68</td>
<td>28</td>
<td>4</td>
<td>0.160</td>
<td>0.0053</td>
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<tr>
<td>1:7</td>
<td>6.3</td>
<td>43.7</td>
<td>421</td>
<td>72</td>
<td>26</td>
<td>1</td>
<td>0.290</td>
<td>0.0097</td>
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<tr>
<td>1:5</td>
<td>8.3</td>
<td>41.7</td>
<td>426</td>
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<td>20</td>
<td>1</td>
<td>0.130</td>
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<tr>
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<td>12.5</td>
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<td>398</td>
<td>82</td>
<td>17</td>
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<td>0.0015</td>
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<td>25.0</td>
<td>414</td>
<td>90</td>
<td>8</td>
<td>2</td>
<td>0.890</td>
<td>0.0296</td>
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<tr>
<td>4.9:1</td>
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<td>8.5</td>
<td>443</td>
<td>94</td>
<td>3</td>
<td>3</td>
<td>0.050</td>
<td>0.0017</td>
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<tr>
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<td>43.7</td>
<td>6.3</td>
<td>440</td>
<td>92</td>
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<td>439</td>
<td>93</td>
<td>3</td>
<td>2</td>
<td>–</td>
<td>–</td>
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Auger electron spectroscopy, combined with Ar⁺ ion sputtering was used to provide a depth profile of the composition. The cylindrical mirror analyzer based Auger electron spectrometer (Perkin Elmer) was calibrated using B₄C, from the boron 179 eV Auger line and the carbon 272 eV Auger line. As can be seen in figure two, the films are very uniform.

![Graph showing atomic concentration of boron, carbon, and silicon against sputter time.](image)

**Figure 2:** An Auger electron spectra depth profile of boron, carbon and oxygen of a boron carbide film fabricated from pentaborane (9) and methane deposited in a 20W of plasma reactor. Percent (atomic) composition is plotted against Ar⁺ ion sputtering time.

**DISCUSSION AND CONCLUSIONS**

The composition of the boron carbide films can be correlated with reaction feed gas mixture used in the rf plasma assisted process, as seen in figure three. The film composition, even accounting for the number of boron atoms in each borane molecule (either 5 for pentaborane or 10 for decaborane), is not linearly proportional to the feed gas composition. The very rich boron films have more carbon than expected while the less boron rich films have far more boron in the films than is expected from an inspection of the gas mixture. This suggests that a number of gaseous or surface reactions occur creating very stable intermediate carborane clusters prior to and during the film formation.

Despite the fact that film composition is not controlled simply from the gas feed mixture, films with a wide range of boron to carbon ratios can be
fabricated. This is consistent with other chemical vapor deposition studies [17,21] where boron carbides from B₃C to B₁₇C have been obtained.

While the boron-carbide films are uniform and can be made free of impurities, the films are, however, polycrystalline. The band gaps of these materials covers a wide range from about 0.8 eV to more than 1.8 eV as will be discussed further elsewhere. These band gaps can be correlated with the boron to carbon ratio [25]. These results and wide range of materials that can be made as outlined in this work hold great promise for these materials in applications where hard semiconductor materials can be employed such as in chemically harsh environments.

![Figure 3: Boron to carbon ratios determined by Auger electron spectroscopy plotted against the ratio of pentaborane (9) to methane partial pressure.](image)

**ACKNOWLEDGEMENTS**

This work was supported by I.B.M. through research agreement 9030, the Air Force through contract no. F30602-89-C-0113, and General Electric Electronics Laboratory.
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