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May 1991

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NOVEL METHODS FOR DEPOSITION OF BORON CARBIDE FILMS

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ABSTRACT

By combining pentaborane (B_5H_9) and decarborane ($B_{10}H_{14}$) 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 BCl_3 reacted with a hydrocarbon (typically methane) [12-16] though variations of this approach using BCl_3 + CCl_4 [17,18] or BBr_3 [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), $B_{10}H_{14}$, 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), B_5H_9, 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 B_4C 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 decarborane 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.

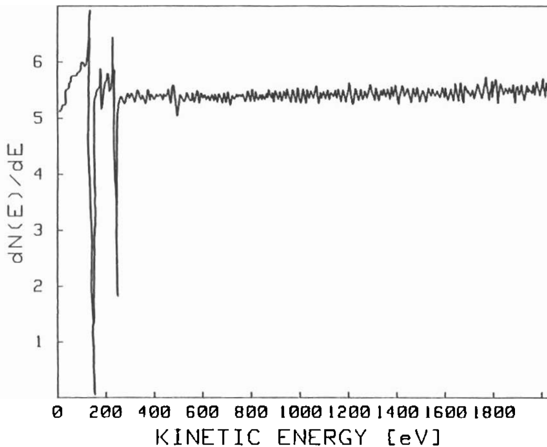

Figure 1: Auger electron spectra of boron–carbide fabricated from 44μ of CH_4 and 6μ of B_5H_9 in a 20 watt rf plasma.

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 $B_{10}H_{14}$ + CH_4

Ratio $B_{10}H_{14}$:CH_4	$B_{10}H_{14}$ Press mTorr	CH_4 Press mTorr	Temp °C	AES Comp B %	AES Comp C %	AES Comp 0 %	Thick-ness μm	Rate μm/min
4.75:1	9.5	2.0	396	<10	50	50	–	–
5.25:1	21.0	4.0	398	15	25	60	0.120	0.0027
7.00:1	35.0	5.0	381	68	20	12	0.040	0.0012
7.00:1	42.0	6.0	398	82	12	6	0.119	0.007

TABLE TWO: SUMMARY OF DEPOSITIONS USING B_5H_9 + CH_4

Ratio B_5H_9:CH_4	B_5H_9 Press mTorr	CH_4 Press mTorr	Temp °C	AES Comp B %	AES Comp C %	AES Comp 0 %	Thick-ness μm	Rate μm/min
1:9	5.0	45.0	449	68	28	4	0.160	0.0053
1:7	6.3	43.7	421	72	26	1	0.290	0.0097
1:5	8.3	41.7	426	78	20	1	0.130	0.0043
1:3	12.5	37.5	398	82	17	1	0.044	0.0015
1:1	25.0	25.0	414	90	8	2	0.890	0.0296
4.9:1	41.5	8.5	443	94	3	3	0.050	0.0017
7:1	43.7	6.3	440	92	4	3	0.400	0.0133
9:1	45.0	5.0	439	93	3	2	–	–

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 B_4C, 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.

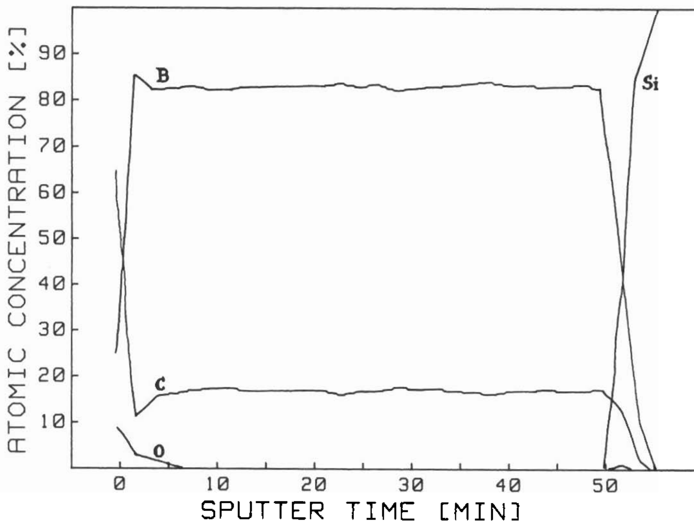

Figure 2: An Auger electron spectra depth profile of boron, carbon and oxygen of a boron carbide film fabricated from pentaborane (9) and methane deposited in a 20W of plasma reactor. Percent (atomic) composition is plotted against Ar^+ ion sputtering time.

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 B_2C to $B_{17}C$ 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.

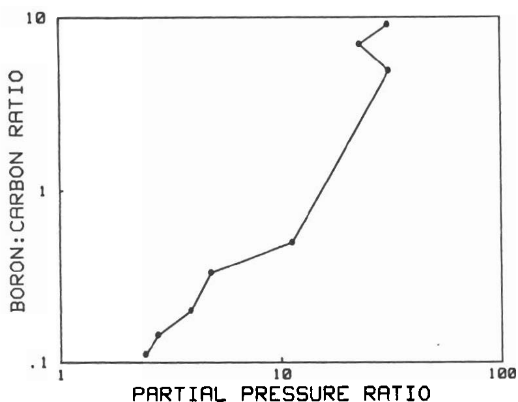

Figure 3: Boron to carbon ratios determined by Auger electron spectroscopy plotted against the ratio of pentaborane (9) to methane partial pressure.

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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