Trimethylboron as Single-Source Precursor for Boron–Carbon Thin Film Synthesis by Plasma Chemical Vapor Deposition

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ABSTRACT: Boron–carbon (B,C) thin films are potential neutron converting layers for 10B-based neutron detectors. However, as common material choices for such detectors do not tolerate temperatures above 500 °C, a low temperature deposition route is required. Here, we study trimethylboron B(CH3)3 (TMB) as a single-source precursor for the deposition of B,C thin films by plasma CVD using Ar plasma. The effect of plasma power, TMB/Ar flow ratio and total pressure, on the film composition, morphology, chemical bonding, and microstructures are investigated. Dense and boron-rich films (B/C = 1.9) are achieved at high TMB flow under a low total pressure and high plasma power, which rendered an approximate substrate temperature of ~300 °C. Films mainly contain B–C bonds with the presence of B–O and C–C, which is attributed to be the origin of formed amorphous carbon in the films. The high H content (15 ± 5 at. %) is almost independent of deposition parameters and contributed to lower the film density (2.16 g/cm3). The plasma compositional analysis shows that the TMB molecule decomposes to mainly atomic H, C2, BH, and CH. A plasma chemical model for the decomposition of TMB with BH and CH as the plausible film depositing species in the plasma is proposed.

INTRODUCTION

Boron carbide is an interesting material due to its high hardness, good wear resistance and low weight, as well as their high thermal and chemical stability.1 Boron carbide is also a potentially interesting semiconductor material where the band gap of boron rich boron carbides, with a B/C ratio of 4–50, has been found to increase with the B/C ratio.2 Furthermore, the isotope 10B is intended to be applied as basis for solid-state neutron converting material for neutron detectors,3,4 given the high neutron absorption cross-section of 10B for thermal neutrons via either reaction 1 or 2 when a neutron is captured by a 10B atom:

\[ ^{10}\text{B} + n \rightarrow ^{7}\text{Li} (0.84 \text{ MeV}) + ^{4}\text{He} (1.47 \text{ MeV}) \]

\[ + \gamma (0.48 \text{ MeV}) \text{ (94\%)} \]  

(1)

\[ ^{10}\text{B} + n \rightarrow ^{7}\text{Li} (1.02 \text{ MeV}) + ^{4}\text{He} (1.78 \text{ MeV}) \text{ (6\%)} \]  

(2)

However, elemental boron has very poor oxidation resistance as well as poor electrical conductivity and thus using pure boron would lead to air sensitive detectors and high charges that build up in the detectors. Therefore, 10B,C thin films are studied as potential neutron converting layers on one or both sides of neutron transparent substrates such as Al or Si.3 For this application, other atoms except 10B inside the thin 10B,C films are potential neutron scatterers, where the magnitude is proportional to the atomic number (Z), thus lowering the performance of the detector. Even though carbon in 10B,C is also regarded as an impurity, it is needed to increase the stability of 10B and provides electrical conductivity. Thus, the 10B-based thin films for neutron detectors should be boron rich (≥80 at. %) and contain as little carbon as possible (≤20 at. %) without compromising the mechanical and electrical properties of the material. Furthermore, any other impurities should be kept at a minimum (<1 at. %). For use in neutron detection applications, crystalline film structure is not required.

Neutron detector-grade boron carbide thin films have been synthesized by magnetron sputtering.3,5 However, magnetron sputtering is a line-of-sight deposition technique. To allow for coating on more complex detector geometries it is worth exploring also chemical vapor deposition (CVD), which can render uniform thin films on more complex surface topologies.

CVD of boron carbides is typically conducted at high temperatures (≥1300 °C) using simple hydrocarbons e.g., CH4 and either chlorides (BCl3) or hydrides (e.g., B2H6) of boron as precursors.6 Boron carbide films can also be deposited from
more complex precursor molecules such as *nido*-pentaborane \((\text{B}_5\text{H}_9)\) and *nido*-decaborane \((\text{B}_{10}\text{H}_{14})\) in combination with methane using plasma CVD at 400 °C resulting in films with B/C ratios 4–50. However, as \(^{10}\text{B}\) based neutron detectors need to be constructed using neutron transparent materials, with Al as the preferred choice from a price and machining point of view, the well-established high temperature and chlorinated CVD processes are not suitable for this application. The penta- and decaborane routes seem promising but will face the challenge of finding boranes enriched in \(^{10}\text{B}\). Another route to decrease process temperature for CVD of boron carbides is to replace the conventional chlorinated precursors with highly reactive, nonchlorinated small organoboron molecules. The organoborons trimethylboron, \((\text{CH}_3\text{CH}_2)_2\text{C}_2\text{B}_4\text{H}_6\) (TMB), triethylboron, \(\text{B}((\text{CH}_3)_2\text{CH})_3\) (TEB), and tributylboron, \(\text{B}((\text{C}_4\text{H}_9)_3\) (TBB), are possible single-source precursors for low temperature thermal CVD of boron carbon films, but until recently only very carbon-rich films has been reported for these using a thermal CVD route. TMB is also reported as a less hazardous substance for deposition of amorphous boron containing films (a-C/B:H). From our experimental results and quantum chemical calculations we suggested a gas phase chemical reaction mechanism in both \(\text{H}_2\) and Ar atmospheres for thermal CVD of B,C films using TEB. However, despite that we could deposit films with a B/C ratio of around 4.5 using TEB, a process temperature above 600 °C was needed to obtain films with a H content below 1 atomic %. A typical route for low temperature CVD is plasma CVD, where energetic plasma species rather than thermal energy are used to activate the film deposition chemistry. This gives potentially rise to different deposition chemistries. Here we explore plasma CVD of B,C thin films using the organoboron TMB as a single-source precursor. As TMB has the highest B/C and B/H ratios of all organoboron precursors it is seemingly the best choice for maximizing the B content and minimizing the H content in the films. TMB is also the only currently commercially available organoboron enriched in \(^{10}\text{B}\).

### Experimental Details

**Film Deposition.** An ASTEX microwave plasma CVD deposition system, equipped with a power supply with maximum output power of 2500 W (Figure 1) is used for the film deposition.

The inner diameter of the chamber is 14 cm, and the diameter of the sample holder is 12 cm, which is neither biased nor grounded. The base pressure in the deposition chamber is lowered to \(10^{-5}\) mbar by a turbo molecular pump. A dry rotary pump is used to pump the process gases during film deposition process and the pressure is controlled either by throttling the rotary pump or by adjusting the gas flow through the CVD system. Ar gas (99.9997% and further purified with a SAES Pure Gas filter) is used as plasma gas and TMB (99.5%, Voltaix/Air Liquide Advanced Materials) is served as single-source precursor supplying both boron and carbon atoms to the deposition process. The outer surface of the quartz dome is cooled with compressed air, while the power supply, magnetron head and chamber walls are water-cooled. For all experiments the plasma power is defined as the set value of power delivered to the microwave generator subtracted by the readout value of the reflected power. The reflected power is minimized by adjusting the tuning stubs shown in Figure 1.

The substrate temperature during deposition is estimated by a thermocouple attached underneath of the graphite substrate holder. It should be noted that this measurement provides an estimate of the substrate temperature during deposition, the substrate surface temperature is expected to be somewhat higher since it faces the plasma but given the very high thermal conductivity of graphite the deviation for the measured temperature is expected to be rather low, on the order of a few tens of °C. The temperature measured over time with the highest studied plasma power (2400 W) using both pure Ar plasma and Ar plasma with 7 sccm TMB is given in Figure 2.

![Figure 1. Schematics of the microwave plasma CVD deposition system.](image)

**Figure 2. Temperature variation of the sample stage with time during deposition process.**

The temperature increases rapidly and stabilizes around 300 °C in both plasmas. A slightly lower temperature can be noted for the Ar + TMB plasma, which can be explained by the consumption of plasma energy by the decomposition of TMB in the plasma.

Full 100 mm diameter (100)-oriented Si wafers are used as substrate material. Prior to deposition, wafers are ultrasonically cleaned with acetone and isopropyl alcohol.

21991
cleaned in acetone followed by isopropanol and blown dry with dry N2 gas. Each process is started by establishing an Ar flow of 45 sccm into the evacuated chamber and igniting an Ar plasma at high power, typically 2400 W, for 15 min to degas the quartz dome and chamber walls. Subsequently, the plasma power and the Ar flow are adjusted to the desired values and TMB is introduced into the chamber, signifying the start of the film deposition. The deposition time is set to 1 h. The samples were allowed to cool down prior to unloading and air exposure for approximately one to 2 h while the plasma CVD system was pumped and purged to remove residual gases from the CVD process.

Two different sets of samples are deposited and characterized. In the first set, the effect of plasma power is studied by depositing films using TMB flows of 5 and 7 sccm in a power range of 700–2400 W. The measured average reflected power is within 0–50 W for all deposition process, thus the plasma power is approximated as the applied microwave power. The Ar flow is kept constant at 45 sccm for all depositions in this set. The total pressure in the chamber was 1.3 ± 0.3 mbar during these experiments, slight variations due to the differences in TMB flow and applied plasma powers are noted. The second set of samples is deposited with increasing Ar flow, 20–70 sccm, at 0.3 ± 0.05 mbar pressure while TMB flow and power are kept constant at 7 sccm and 2400 W, respectively.

**Film and Plasma Characterization.** All deposited films are characterized with time-of-flight elastic recoil detection analysis (ToF-ERDA) using 36 MeV iodine ions for compositional analysis. More experimental details of the ToF-ERDA can be found elsewhere.\(^1\) Scanning electron microscopy (SEM) is carried out for morphological analysis, as well as to determine film thickness using a Philips X-ray diffractometer in HR rocking curve geometry. The radius of the substrate curvature was calculated using

\[
R \approx \frac{\Delta x}{\Delta \omega [\text{rad}]}
\]

in which \(\Delta x\) is the distance between two measured positions \(x\) on the sample surface and \(\Delta \omega\) is the small difference between the peak centers (\(\omega\)) detected at the corresponding \(x\)-positions. The compressive stresses are then calculated using the Stoney equation:

\[
k = \frac{1}{R} = \sigma t_f - \frac{6}{M_E t_s^2}
\]

where \(t_f\) and \(t_s\) are film and substrate thickness, respectively. The biaxial modulus of the substrate is \(M_s = E_s/(1 - \nu_s)\), \(E_s\) is the elastic modulus of substrate, and \(\nu\) is Poisson’s ratio. The same diffractometer is also used for X-ray reflectivity (XRR) measurements. A \(\omega/2\theta\) scan is recorded for all samples by using hybrid mirror optics with a 2-bounce Ge 220 triple-axis crystal analyzer. The experimental data are simulated and fitted using Xpert reflectivity software to determine film densities by assuming the three layers from the film to substrate: B4C, SiO2, and Si, respectively. The chemical composition and bonding states of B,C films are investigated by X-ray photoelectron spectroscopy (XPS, Axis UltraDLD, Kratos Analytical, Manchester, U.K.) using monochromatic Al (K\alpha) X-ray radiation \((h\nu = 1486.6\ eV)\). XPS survey spectra and core level spectra of the B 1s, Ar 2p, C 1s, and O 1s regions are recorded in the Fermi edge are recorded on as-received samples. After sputter cleaning with a 500 eV Ar\(^+\) beam rastered over an area of 3 \(\times\) 3 mm\(^2\) at an incidence angle of 20° for 10 min, the B 1s, Ar 2p, C 1s, and O 1s regions are recorded again. Automatic charge compensation is applied throughout the acquisition. In order to assess the bonding configuration of the B,C films, the core level spectra are deconvoluted using a Voigt peak shape with a Lorentzian contribution of 30%. The full width at half-maximum (fwhm) of the components are restricted to 2 eV and referenced to the C–C sp\(^3\)/C–CH signal at a binding energy of 284.5 eV. The Raman spectra of the samples are collected using a micro-Raman setup with an objective of magnification of 100×. The power of the exciting laser at 532 nm is kept at ~0.5 mW in order to avoid thermal-induced changes or damage in the films. The spectra are recorded using a single monochromator coupled to a CCD camera with resulting spectral resolution ~5 cm\(^{-1}\). The optical emission spectroscopy (OES) measurements are done for both pure Ar and Ar + TMB plasma to study the plasma composition, i.e., excited and ionized atoms, as well as radicals from dissociation of precursor molecules in the plasma using a spectrometer Mechelle Sensicam 900 with a spectral resolution \((\Delta \lambda)_{\text{fwhm}}\) of 900 by Multichannel Instruments. Emission spectra are recorded in a wavelength range from 200 to 1100 nm.

### RESULTS AND DISCUSSION

**Effect of Plasma Power on Film Deposition.** SEM images show that the film thickness varies significantly from the center to edge over the Si wafer, thicker at the center and thinner toward the edge, as shown in Figure 3, parts a and b,

![Figure 3](image)

Figure 3. Cross-sectional SEM images of film thickness at (a) center and (b) outer region of a 100 mm diameter Si(100) wafer. Indicated are the film and substrate as well as the film thickness. TMB flow and plasma power are set to 7 sccm and 2400 W, respectively, at a total pressure of 1.6 mbar.

respectively. This can be explained by the expected gas flow pattern inside the chamber (Figure 1). The gases are introduced at the side of the semispherical quartz dome and flow toward the top of the dome. At the top of the dome, the gas flow redirects down toward the center of the substrate and spreads out on the surface toward the edge and is pumped out below the substrate. Thus, the highest flux of film forming species is expected in the center of the substrate and results in the highest deposition rate in the center of the wafer. As the gas flows over the wafer, the species are consumed and contribute to a lower growth rate toward the wafer edge. The films appear porous when deposited at high TMB flow and high plasma power. The film porosity is likely an effect of the high flux of
film forming species, possibly also in combination with too low adatom mobility, resulting in a high deposition rate: \(\sim 8.4 \, \mu m/h\) at 7 sccm TMB and approximately 2400 W, Figure 3a. As this study aims to understand the deposition process rather than the film uniformity, only the center area of the wafer has been used for further characterization.

The elemental composition of the films is found to be dependent on the TMB flow and plasma power, as shown in Figure 4 and Figure 5. Samples deposited with a lower TMB flow, 5 sccm, are C-rich, regardless of plasma power, while samples deposited with a TMB flow of 7 sccm are B-rich when deposited at plasma powers >1400 W. When samples are deposited with 5 sccm TMB, the significant increase in C content at higher plasma powers is likely due to different plasma chemistry in the gas phase resulting in different carbon-rich film forming species. It is interesting to note that no such turning point with respect to C content is observed when films are deposited with 7 sccm TMB flow. This can indicate that even at elevated powers, a higher TMB flow consumes most of the plasma energy. In consequence, the plasma chemistry in which the carbon-rich species are formed and/or the favorable surface chemistry for C deposition is not created. For the higher TMB flow, the C content decreases while the B content shows a steady increase with increasing plasma power. This suggests that a larger supply of boron species is produced as the TMB flow increases, since the surface chemistry is not expected to be significantly altered by the higher TMB flow into the plasma. The TMB flows higher than 7 sccm could not be used because the maximum output power of 2500 W is insufficient to sustain the plasma discharge due to the decomposition of TMB molecules consuming the plasma energy.

Comparing the amounts of incorporated H and O in the films deposited at 5 and 7 sccm TMB flow for the different power settings (cf. Figure 4 and Figure 5), it is evident that the plasma power effects the impurity levels of the films depending on the TMB flow. At a TMB flow of 5 sccm, the H content drops from 19 to 10 at. % as the plasma power is increased from 700 to 1750 W. For films deposited at a TMB flow of 7 sccm, the plasma power does not appear to affect the H content, and it is almost constant at 19 ± 2 at. %. The results described above regarding to B, C, and H contents indicate that the possible film forming species in the plasma are mainly CHx and BHy. It should also be noted that films appear more porous with higher TMB flow and high plasma power, which increases the possibility of surface contamination by exposure to the atmosphere that can account for some of the measured H and O in the films.

The O contamination in the films shows a strong dependence on plasma power. For both TMB flows, the O content decreases with increasing plasma power, suggesting that the higher plasma power helps one to prevent O incorporation. A possible source for O contaminants is adsorbed water and dioxygen from exposing the inside of the deposition chamber to air when loading and unloading samples. A higher plasma power during deposition should lead to a higher degassing rate of the chamber walls. Oxidation of the films after exposure to air can also be a source of at least some of the detected O given that the films are comparatively porous.

**Effect of Pressure on Film Deposition.** The samples deposited at varying plasma power, described above, are found to be porous. From well-known CVD structure/property/process relationships, a lower concentration of precursors (supersaturation) should lead to deposition of less porous films at the same temperature. Therefore, in a second set of experiments, the TMB flow and plasma power are kept at the set points that provided the best films in terms of elemental composition (TMB, 7 sccm; plasma power, 2400 W), while the total pressure during deposition is lowered to 0.3 ± 0.05 mbar. For these experiments, the TMB partial pressure is lowered approximately 1 order of magnitude by a lower total pressure, which was achieved by increasing the pumping speed. The TMB partial pressure is further adjusted by varying the diluting Ar flow from 20 to 70 sccm. Here, the plasma power is slightly changed as the reflected power varied by 400 ± 100 W depending on the Ar gas flow. SEM images in Figure 6 show that the films become denser with the lower TMB partial pressure and total pressure compared to the first set. Moreover, the microstructure changes from coarse-columnar to more smooth when the Ar flow is increased. The deposition rates are ranging between 1 and 2 \(\mu m/h\), which is 4–8 times lower, compared to the first set of samples (cf. Figure 3).

Elemental compositional analysis by ERDA (Figure 7) shows that the relative amount of B in the film reached 55 at. % when films deposited at lower Ar flow (20 and 30 sccm) which is 8 at. % higher than the highest B content obtained from the first set of samples. A slight decrease of B content to 50 at. % is
The C content remains at 30 ± 1 at. % for all deposited films. The H content shows a slight increase (17 ± 2 at. %) while the O content decreases from 1.2 to 0.3 at. % with the increasing Ar flow. A possible explanation for the lower O content is that the denser microstructure allows less oxidation upon exposure to air.

Despite the changes in the film morphology, Figure 6 shows that films, except the one deposited at 20 sccm Ar flow, delaminates from the substrate. In addition to the surface delamination, surface cracks can be noticed for the thickest film (2 μm) deposited at 30 sccm Ar flow. These observations suggest that films experienced compressive stresses. HR-XRD rocking curve measurements revealed that residual stress levels in the films range between 80 and 350 MPa. The lowest stress of 80 MPa is obtained for the film, which has both delamination and surface cracks. The other two films with only delamination have a stress value of 350 MPa, while the film without any delamination or cracks shows a residual stress of 270 MPa. However, since stresses are calculated measuring substrate curvature, values obtained from samples with delamination and cracks cannot be considered as the actual residual stresses in the films. The SEM images and calculated stresses, suggest that the increased Ar flow (>20 sccm) during deposition increases formation of compressive stresses due to the increased number of energetic plasma species bombarding film surface resulting in poor film adhesion. The improved adhesion of the film deposited at a low Ar flow of 20 sccm can be related to its coarse columnar morphology, as the columnar structure is preferable to provide an efficient stress relaxation mechanism caused by the different thermal expansions between the substrate and film.\(^\text{15}\)

The densities for the films shown in Figure 6 are 2.16 ± 0.01 g/cm\(^3\), which is 87% of the bulk density for crystalline B\(_4\)C: 2.52 g/cm\(^3\),\(^\text{16}\) and almost regardless of microstructure of films, i.e., whether a columnar structure (a) or more merged structure (c, d). Therefore, the microstructure independent low film density is associated with the high H incorporation in the films.

**Chemical Structure of Deposited Films.** The films shown in Figure 6 are analyzed by XPS. B 1s and C 1s core level spectra, shown in Figure 8 are obtained before and after sputter cleaning with 500 eV Ar\(^+\) ions. The B 1s spectra (Figure 8a–d) are fitted using three components assigned to B–B (188.15–188.2 eV), B–C (188.7–189 eV), and B–O (190.5–191 eV). The component assigned to B–C bond centered at a binding energy of 188.85 ± 0.15 eV is dominating and close to the reported B–C binding energies for B\(_4\)C and BC\(_3\),\(^\text{17,19}\) which range between 188.4 and 188.9 eV, respectively.\(^\text{17}\) The peak assigned to B–O at 190.75 eV ± 0.25 eV\(^\text{18}\) is significantly reduced after sputter cleaning (not shown in Figure 8), suggesting that surface oxides are formed upon exposure to air. In addition to peaks resembling B–C and B–O bonds, one more component at 188.15 ± 0.05 eV is observed and matched well with the reported binding energy of B–B bonds.\(^\text{17,19}\)

For the films deposited with 20 and 30 sccm Ar, the C 1s spectra shows double peaks (cf. Figure 8, parts e and f), while films deposited with 45 and 70 sccm Ar flow show a single broad peak featuring a shoulder (cf. Figure 8, parts g and h). The components are assigned to C–B bonds (at 282.45 ± 0.05 eV) and C–C bonds (at 284.45 ± 0.05 eV). The shift of 0.1 eV for the C–C binding energy is due to nearest-neighbor effects (secondary chemical shift), where the C–C binding energy is affected by the bond type of neighboring C atoms. The full width at half-maximum (fwhm) of components arising due to B–B, B–C, C–C, and C–B bonds is <1.6 eV. The broadened fwhm arise due to the amorphous nature of the films. Here, repeating unit cells, leading to well-defined binding energies assigned to one bond type are lacking.

Parts a and b of Figure 9 display the Raman spectra obtained from the central region (Figure 9a) and the outer region (Figure 9b) of the sample deposited in the first set (as shown in the SEM image in Figure 3), while the Raman spectra for the dense films in the second set deposited at different Ar flows are shown in Figure 9c–f (the corresponding SEM images are displayed in Figure 6). The central region of the sample in Figure 3a shows a spectrum with two well-separated bands peaking at 1587 cm\(^{-1}\) (G band) and 1350 cm\(^{-1}\) (D band), respectively (cf. Figure 9a). The spectrum is typical for amorphous carbon suggesting its formation in the film due to the relatively high C content of 41 at. % in the central region of the sample. The disorder introduced in the carbon matrix by other incorporated atoms, mainly B (47 at. %), H (8.3 at. %), and O (3.4 at. %) may be reflected in the relatively large fwhm

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**Figure 6.** Cross-sectional SEM images of films deposited at different Ar flows at a total pressure of 0.3 mbar. The TMB flow and the plasma power are set to 7 sccm and 2400 W, respectively.

**Figure 7.** Composition of B\(_4\)C films (with the calculated B/C ratio) as determined by ToF-ERDA measurements for films deposited at different Ar flows.
of the D and G peaks. The spectrum taken from the outer region of the same sample (Figure 9b) shows much broader nearly coalescing D and G peaks with significantly red-shifted G band. The red shift of the G peak suggests weakening of the sp² bonds in the carbon matrix, which may be due to the lower C content (∼37 at. %) and the higher H content (16.5 at. %) in the outer region of the sample compared to that in the central region. The broadening of the carbon-related peaks (G and D) also indicates increased disorder resulting from reduced size of the amorphous carbon phase in the film and higher H-content.

Considering the more dense films (SEM image in Figure 6), their Raman spectra exhibit significant downshift of the G and D peaks (Figure 9c–f) compared to the positions of the corresponding bands in the films deposited in the first set. Some of the samples (e.g., those deposited at 30 sccm Ar flow in Figure 9c) show a shoulder at the position expected for the G band, but essentially the spectra of all samples (except the central region of the sample in Figure 9a) are dominated by a band peaking at about 1490 cm⁻¹ and another low-energy band peaking at about 1220 cm⁻¹. The downshift of the peaks suggests weakening of both sp² and sp³ matrix, which might indicate formation of amorphous carbon inclusions with even smaller size than in the films deposited in the first set (Figure 3 and Figure 9a,b). However, the Raman spectra for films deposited at 70 and 20 sccm Ar flow, spectra d and f, respectively, are almost flat in the region of the G and D bands, which indicates that very low amount of free carbon formed in the films. However, such an indication is uncertain for spectra d due to the high background (photoluminescence) intensity.

**Plasma Chemistry.** The OES spectra of pure Ar plasma show mainly emission lines from excited Ar atoms (Ar I) at 700–860 nm while the emission lines after inserting TMB appear mainly in the visible range (400–670 nm) as shown in Figure 10.

In Figure 10, OES spectra of the plasma with (a) low TMB flow and plasma power (∼1750 W) and (b) high plasma power (2400 W) are shown.
TMB flow and high plasma power (7 sccm and ~2400W) show that no additional TMB related emission lines appear with the increasing plasma power and TMB flow—it is only the intensity of the TMB related emission lines that changes with power and flow. It should be noted that almost all Ar I lines (not shown in Figure 10) are significantly more intense than any of the other emission lines from the plasma. This suggests that the excited Ar atoms dominate the overall plasma. The emission lines related to the decomposition products of TMB (Figure 10), are dominated by lines from BH, CH and atomic H. The double lines at 431.5 and 430.6 nm are assigned to CH with a ~ 1 nm blue shift compared to the listed values (432.4 and 431.2 nm)20 due to an instrumental error. The H$_4$ and H$_3$ lines at 657.7 and 486.4 nm, respectively, are clearly seen while H$_2$ at 434.1 nm overlaps with the BH line at 433.6 nm due to the low resolution of the spectrometer.21 In addition, intense emission lines at 514.5 and around 600 nm are identified as C$_2$ swan band ($\Delta v = 0$), molecular H$_2$ and C$_2$ ($\Delta v = -2$), respectively.20,22,23 A weak emission from C$_3$ is observed close to the violet.19,21

On the basis of the presence of BH, CH, H, C$_2$ and C$_3$ but absence of B ($\sim$249 nm) and CH$_4$ (within 138 – 217 nm) in the plasma, we suggest that the TMB molecule decomposes by dehydrogenation of the methyl groups

$$\text{B(CH}_3)_3 \rightarrow \text{B(CH}_2)_2(\text{CH}) + 2\text{H}^*$$  (5)

likely assisted by excited Ar atoms/thermal energy in the plasma, followed by breakage of the B–C bonds to form CH radicals

$$\text{B(CH}_2)_2(\text{CH}) \rightarrow \text{B(CH}_2)_2 + \text{CH}$$  (6)

at least one B–C should be broken by a hydrogen radical to form the BH radical

$$\text{B(CH)} + \text{H} \rightarrow \text{BH} + \text{CH}$$  (7)

C$_3$ can form either by reaction of *CH radicals

$$2\text{CH} \rightarrow \text{C}_2 + \text{H}_2$$  (8)

or by further dehydrogenation of *CH radicals followed by combination of atomic carbon. The direct reaction of two *CH radicals seems more likely given the stable byproduct H$_2$. The C$_2$ and C$_3$ carbon clusters are a likely source for the formation of amorphous carbon phases in the films as shown by our XPS and Raman measurements. It is also reasonable that the formation of carbon clusters is enhanced by higher plasma power while the TMB flow is 5 sccm, as shown in Figure 4. A higher formation of C$_2$ at higher plasma power can also explain the lower hydrogen content in the films at higher plasma power (Figure 4) as the film will mostly be deposited also by C$_2$ and C$_3$ than by CH. The existence of BH and CH bands and their high concentration at high TMB flow and plasma power can be correlated to the increase in B content, as well as the high H content (19 ± 2 at. %) in the films. Therefore, CH and BH are proposed to be the most likely film depositing species in the plasma.

**CONCLUSIONS**

Trimethylboron (TMB) is shown to function as a single-source precursors in plasma CVD of B$_4$C films on Si substrates. XPS analysis shows that the films contain mainly B–C and C–B bonds and to lower extent B–O as well as C–C bonds. B–O bonds were mainly found on the film surface and thus attributed to air exposure, while observed C–C bonds are primarily attributed to the formation of amorphous carbon phases in the films. Raman spectroscopy further confirms presence of amorphous carbon in the films. The partial pressure of TMB and the total pressure during deposition are found to be crucial for depositing dense and B-rich B$_4$C films. However, only a B/C ratio of 1.9 is achieved for the investigated CVD settings. The H content in the films ranges between 10 and 20 at. %, and has not been significantly reduced by any deposition parameters. The O content in the film is reduced to <1 at. % with increasing plasma power likely as a result of degassing absorbed water and dioxygen from the chamber walls and the improved microstructures. Films with a dense microstructure show compressive stresses of less than 300 MPa and a density of 2.16 ± 0.01 g/cm$^3$. OES analysis shows that the plasma composition after inserting TMB mainly contains atomic H, C$_2$, CH and BH bands, and based on the film composition it is proposed that CH and BH most likely contribute to the film formation. The deposited B$_4$C films are not fully suitable as neutron converter films due to their high hydrogen content and moderate B/C ratio, however, this study points to the possibility to deposit more carbon rich boron–carbon films compared to plasma CVD routes based on penta- and decaboranes. Such films with a higher carbon content but without graphite inclusions are potentially interesting as semiconductors.

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Notes

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