Modeling and diagnostics of microwave discharges (H₂/CH₄ and H₂/CH₄/B₂H₆) used for diamond and boron-doped diamond deposition.

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Abstract: High power electronic industry needs high quality boron doped p-type semiconducting diamond that can be grown by microwave plasma operating in H₂/B₂H₆/CH₄ mixtures and at high power density. The understanding of the processes involved in this kind of plasma needs to develop a research based on plasma modeling as well as spectroscopic analysis, the goal in particular being identifying the boron containing species responsible for boron diamond doping. A thermochemical modeling for describing H₂/B₂H₆/CH₄ mixture discharges is developed. It includes a rather detailed chemical kinetics model for carbon and hydrogen containing species, and a simpler B-species model involving only BHₓ species (x=0-3). Calculations draw up spatial profiles of gas and electron temperatures, as well of different species densities. The conditions of very high power density (power > 3 kW, pressure > 200 hPa) that have been little studied so much are also investigated here. Spectroscopic measurements, carried out in H₂/CH₄ mixtures, are compared to simulations, allowing us to draw some conclusions on the atomic hydrogen and electron temperature at high power density.

Keywords: microwave plasma, diamond deposition, modeling, emission spectroscopy, actinometry.

1. Introduction
Among all the wide band gap semiconductors, synthetic single crystal diamond has the most significant potential for being used in the field of power electronics [1]: a wide band gap (5.5 eV) and a theoretical breakdown voltage of up to 10 MV.cm⁻¹. It is also characterized by a hole mobility as 4500 and 3800 cm².V⁻¹.s⁻¹ (measured at 25°C) [2-3]

However, these applications require high purity and high quality thick diamond films synthesis implying growing films at high grow rate under a very clean environment. These requirements are achieved using a microwave enhanced chemical vapour deposition (CVD) process under conditions of high power density (high pressure and high microwave power) [4]. Thus, in our experimental conditions, typical grow rates of around 20 µm/h [5] are currently reported although a value of up to 70 µm/h has been reached.

Although n-type doping is still difficult to obtain due to the lack of an efficient donor, p-type doping can now be reliably achieved using boron as an acceptor impurity, thus potentially opening the way to the
fabrication of unipolar power devices, entirely made in diamond.

In our lab, the p-doping diamond has been achieved using $\text{H}_2/\text{CH}_4/\text{B}_2\text{H}_6$ gas mixture. It was observed that for a given concentration of boron into the gas phase, the doping efficiency increases significantly with the decreasing of the microwave power density (MWPD), probably due to the decrease in the diamond quality. At high MWPD, boron concentration measured by secondary ion mass spectrometry (SIMS) saturates to values around $5\times10^{19}$ cm$^{-3}$, prohibiting to reach the metallic transition ($>10^{20}$ cm$^{-3}$) [6]. Although appropriate conditions have been find to grow high quality metallic boron doped layers, one of our goals now is to grow highly boron doped layers at very high power density.

Understanding and controlling the complex chemistry which occurs within the plasma and leads to doping is very important, in particular in order to identify the boron doping key species [7]. In the next part, experimental and numerical tools will be developed. Then spectroscopic measurements in $\text{H}_2/\text{CH}_4$ plasmas are presented for different power density conditions, and compared with numerical simulations. Finally, calculations performed in $\text{H}_2/\text{CH}_4/\text{B}_2\text{H}_6$ gas mixture are reported.

2. Experiment - Modeling

The CVD processes involve many complex phenomena which are strongly coupled. Modeling contributes to the understanding of various phenomena occurring during the film’s growth.

Modeling of the discharge has been developed using a 1D axial model, from the substrate to the top of the reactor, which describes the chemistry of the plasma and the specie’s transport by diffusion [8].

In order to study $\text{H}_2/\text{CH}_4/\text{B}_2\text{H}_6$ gas mixture, the kinetic scheme composed by the four reactions below has been implemented:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>reference</th>
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<tbody>
<tr>
<td>1 $\text{B}_2\text{H}_6 + \text{H}_2 \leftrightarrow 2\text{BH}_3 + \text{H}_2$</td>
<td>[7]</td>
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<tr>
<td>2 $\text{BH}_3 + \text{H} \leftrightarrow \text{BH}_2 + \text{H}_2$</td>
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<td>3 $\text{BH}_2 + \text{H} \leftrightarrow \text{BH} + \text{H}_2$</td>
<td>[7]</td>
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<tr>
<td>4 $\text{BH} + \text{H} \leftrightarrow \text{B} + \text{H}_2$</td>
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Spectroscopic measurements have been done on a microwave cavity based plasma reactor (Fig. 1) running at pressure typically in the range from 100 to 270 mbar with some kilowatts power coupled to the plasma in the range from 2000 to 4000 W. $\text{CH}_4$ concentration of 4% is used. Actinometry measurements were performed with 3% of argon as an impurity in the feed gas [10]. An Acton 2500i spectrometer equipped with an ICCD camera was used to perform emission spectroscopy. The optical collection enables a spatial resolution of 1 mm and a spectral resolution of 0.03 nm. The optical system was mounted on computer controlled translation stages allowing axial measurements.

Figure 1: Schematic of the microwave reactor and the experimental set-up
3. Results

Measurements of the H atom mole fraction are deduced from the emission intensity ratio of the Hα line (656 nm) and the 750 nm argon line using the equation:

\[
\frac{[H]}{[Ar]} = \frac{x_H}{x_{Ar}} = F \cdot \frac{k_e^{Ar^*}}{k_e^{H\alpha}} \cdot \frac{v_{Ar^*}}{v_{H\alpha}} \cdot Q_T \cdot I_H / I_{Ar}
\]

Where \(k_e^{Ar^*}\) and \(k_e^{H\alpha}\) are excitation rate constants for the transition Ar(3p)→Ar(4p) and H(n=1)→H(n=3); \(v_i\) is the de-excitation frequency of species \(i\); \(x_i\) is the mole fraction of species \(i\); \(Q_T\) is the term relative to radiative and quenching processes and \(F\) is an optical device factor [10-11].

The electronic temperature has been provided from measurements of the emission intensity ratio of the Hα line (656 nm) and the Hβ line (486 nm).

The variation of the electronic temperature as a function of the power density is shown in Figure 2. A decrease from 17000 K to around 10000 K is observed as the pressure is increased from 14 mbar to 270 mbar.

The variation of H mole fraction as a function of the pressure for different powers coupled to the plasma is shown in Figure 3. A strong increase in the H-atom mole fraction is observed: it rises from 0.01 at 25 mbar and 600 W (the reference) up to around 0.6 at 270 mbar and 4000 W.

It is worth noting that the quenching has to be taken into account due to the high pressure. Furthermore the electron temperature and the H atom mole fraction were calibrated on the basis of calculations [9].

Red crosses on figures 2 and 3 correspond to the 1D axial model calculations. These results are in very good agreement with the experiments.

![Figure 2: Electron temperature fractions as a function of pressure for different powers](image1)

![Figure 3: H mole fraction fractions as a function of pressure for different powers](image2)

It was also previously demonstrated that the gas temperature (Tg) increases with the MWPD for H\(_2\)/CH\(_4\) plasmas [12], and that there is no variation of Tg for a given power density as a function of the addition of B\(_2\)H\(_6\) in the gas mixture [7].

Numerical results given from the 1D axial code using the simple kinetic model \(BH_x + H \leftrightarrow BH_{x+1} + H_2\) (\(x=0\)-3), are presented in Figures 4.

These results show that in the plasma phase where the temperature is high, the reaction
BH$_x$ + H $\leftrightarrow$ BH$_{x+1}$ + H$_2$ is strongly shifted to the right. This induces a strong production of B atoms and a consumption of BH$_x$ species. However, near the substrate, where the gas temperature is lower, BH$_x$ radical densities are seen to increase in this region at high power density as has been observed for CH$_3$ [12].

This model will be completed in the near future with reactions taking into account the interaction between carbon and boron containing species in order to identify mechanisms responsible for the doping process. Furthermore emission spectroscopy and laser induced spectroscopic measurements on boron containing species, will be also carried out to validate the model.

![Figure 4](image)

**Figure 4:** Density of the boron containing species as a function of the axial position for [B] / [C] = 2000 ppm, [CH4] = 7%, Pressure 200 mbar, Power microwave 3000W

**References**


