

INVESTIGATION OF H₂/CH₄ AND H₂/CH₄/B₂H₆ HIGH PRESSURE-HIGH POWER MICROWAVE PLASMA CHEMISTRY USING IR-TDLAS

C. ROND¹, S. HAMANN², M. WARTEL¹, G. LOMBARDI¹,
K. HASSOUNI¹, A. GICQUEL¹, J. RÖPCKE²

¹ LSPM-CNRS, Villetaneuse, 93430, France

² INP-Greifswald, Greifswald, 17489, Germany

*cathy.rond@lspm.cnrs.fr

ABSTRACT

Infrared tunable diode laser absorption spectroscopy (IR TDLAS) technique [1,2] has been used in a high pressure microwave (2.45 GHz) stainless steel reactor dedicated to diamond films deposition for electronic applications. Line integrated absorption measurements have been performed in H₂/CH₄ and H₂/CH₄/B₂H₆ plasmas in order to monitor hydrocarbon species (CH₃, CH₄, C₂H₂, C₂H₄ and C₂H₆) and diborane (B₂H₆). The densities of the detected species were in the range of 10¹² – 10¹⁷ cm⁻³. Parametric studies as a function of pressure-microwave power couple and gas composition (admixture of methane and diborane) have been carried out on wide ranges of experimental conditions, especially for high pressure (≥ 200 mbar) and high power (≥ 3 kW). The results show an increase of the degree of dissociation of CH₄ and B₂H₆ with pressure and power. C₂H₂ is the most abundant reaction product. The concentration of CH₃ within the plasma bulk was detected to about 10¹³ cm⁻³ and only for the lowest power density conditions. In the presence of methane the concentration of diborane is below the limit of detection of about 5·10¹¹ cm⁻³.

1. INTRODUCTION

The synthesis of high quality single crystal diamond, intrinsic or doped layer, by microwave plasma assisted chemical vapour deposition (MW-PACVD) has opened up the opportunity to make efficient diamond-based electronic devices. One of the key issues associated with high purity diamond growth at high deposition rates is the use of high pressure and high MW power conditions, *i.e.* high power density [3]. Understanding in order to master the MW-PACVD process in these conditions of high power density is of great interest to answer these

requirements. It is therefore essential to understand chemistry and transport phenomena of the H₂/CH₄ and H₂/CH₄/B₂H₆ plasma for these experimental conditions. Different plasma diagnostics have been employed in the stainless steel reactor working at high power density.

Optical Emission Spectroscopy (OES) measurements have allowed determining H-atom density and electron and gas temperature. Microwave interferometry technique has been achieved to measure the electron density of the plasma [4,5]. Previously used in the Bell Jar reactor configuration for moderate power density, Infra-Red absorption spectroscopy is among the most efficient non-invasive tool for polyatomic species detection as carbon-containing species or diborane.

The aim of this paper is to present IR Tunable Diode Laser Absorption Spectroscopy measurements of H₂/CH₄ and H₂/CH₄/B₂H₆ plasma for a wider range of diamond growth conditions, [25-270] mbar and [600-4000W].

2. EXPERIMENTAL SET UP

The microwave (MW) diamond deposition reactor, a water-cooled stainless-steel chamber forming a resonant cavity at 2.45 GHz [4,5], is equipped with a White cell multiple pass optical arrangement and coupled to a transportable tunable infrared multi-component acquisition system (IRMA) [2,6]. The plasma, formed on the top of a 5 cm in diameter substrate holder, represents only 8% of the optical paths (60 cm multi-pass cell long) (Fig.1).

The total pressure in the reactor chamber and the MW power are coupled in order to maintain the ratio of the power absorbed by the plasma over the total density constant, and so the plasma volume. The pressure ranges from 25 mbar to 270 mbar and the power increases simultaneously from 600 W to 4000 W.

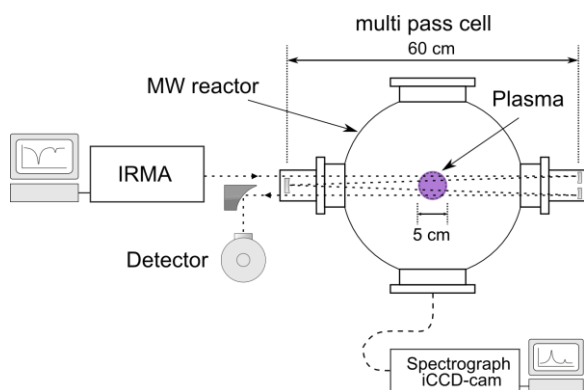


Fig. 1 Experimental set-up

Two campaigns have been performed. The measurements are interpreted with the help of a 1D radial model [7]. Indeed, the fitting procedure of the IR lines relies on the Beer-Lambert law. Species density can be estimated from the absorption signal for a known gas temperature and a known absorption length. The application of this method is sensitive in this process because the gas does not constitute a homogeneous medium at uniform temperature. However, despite stiff gradients within the chamber, modelling allows defining areas where temperature and densities can be considered uniform. In this way, absorption lengths of stable species (C_2H_2 , C_2H_4 , C_2H_6 , CH_4 , B_2H_6) are estimated to be equal to the total optical path whereas for the radical (CH_3) the characteristic length is close to the plasma diameter (5 cm).

For the first campaign, the feed gas composition consists in few percent of CH_4 (0-7%) diluted in hydrogen. Four passes were realized through the White cell arrangement leading to an optical length inside the reactor of about 2.4 m. Measurements have been mainly carried out at $Z=1.6$ cm above the substrate, that is in the plasma bulk, and few additional experiments have been achieved at $Z=1.2$ cm. The second experimental campaign deals with $H_2/CH_4/B_2H_6$ mixtures where methane is varied in the range of [0-5]% and diborane content ranges from 30 to 165 ppm. The total optical length was equal to 12 m (20 passes) and the line of sight of measurements was $Z=1.5$ cm above the substrate. More details on IR TDLAS investigations are reported in [2,6].

4. H_2/CH_4 PLASMA

The absorption lines used for concentration measurements, their position and line strengths are listed in table 1.

Table 1. IR absorption lines

Species	Position [cm^{-1}]	Line-Strength [molecules. cm^{-1}]	Ref
CH_4	1313.722	5.596×10^{-22}	[8]
CH_3	612.413	2×10^{-20}	[2]
C_2H_2	1314.068	3.650×10^{-20}	[8]
C_2H_4	2994.091	3.795×10^{-21}	[8]
C_2H_6	2993.472	1.980×10^{-20}	[8]

The absorption spectra process requires defining an average temperature along the optical path for each species.

The gas temperature corresponding to the stable species area has been measured from the CH_4 absorption spectra using the Boltzmann plot method. We note that the average gas-reactor temperature (out of the plasma) increases with the pressure-power couple from 340K at (30 mbar-600W) to 410 K at (270mbar-4000W). This evolution results mainly from transport phenomena (heat and mass diffusion) that reveal the increase of the plasma bulk temperature when the pressure-power couple increases.

The average temperature corresponding to the CH_3 area is estimated from Doppler broadening measurements of the CH_3 absorption line. The production of CH_3 is located in the plasma bulk for conditions of low power and pressure. The CH_3 temperature is measured close to 3000 K ($\pm 500K$) for low power density (50 mbar – 1000W) which is in relatively good agreement with OES measurements [4].

Integrated measurements of species density and species mole fractions are presented in Figure 2 and Figure 3 respectively. CH_4 , C_2H_2 , C_2H_4 and C_2H_6 have been measured for pressure-power couples from 25 mbar – 600 W (50 mbar-1000W for C_2H_4) to 270 mbar – 4000W whereas the methyl radical has been detected up to 70 mbar – 1500 W. At high power density the concentration of CH_3 was below the limit of detection of the IR system (about $10^{13} cm^{-3}$). We note that for this range of pressure and power, CH_4 density is quite constant ($1 - 2 \times 10^{16} cm^{-3}$); however, density of C_2H_y ($y=2,4,6$) highly increases with pressure and power conditions. Moreover, we observed that methyl density decreases when the pressure-power couple increases (Fig.2).

Regarding the CH_4 mole fraction which decreases from 0.15×10^{-2} (25 mbar-600W) to 2×10^{-3} (270 mbar-4000W), it is to say that the dissociation rate of methane rises with the pressure-power conditions. This evolution is mainly due to the gas temperature increase

because of higher MW power. In the same way, within the plasma bulk, methyl radical mole fraction strongly decreases with pressure-power conditions from 2.3×10^{-4} at 25 mbar – 600 W to 3.1×10^{-5} at 70 mbar – 1500 W; whereas C_2H_6 mole fraction is almost constant at about 1×10^{-4} whatever the pressure-power couple. C_2H_4 mole fraction shows a slight increase from 9×10^{-4} at 50 mbar-1000 W to 2×10^{-3} at 270 mbar-4000 W; and C_2H_2 mole fraction also increases from 2.4×10^{-3} at 25 mbar-600 W to 1.3×10^{-2} at 270 mbar-4000 W. The results obtained for low pressure-power conditions (up to 100 mbar-2000 W) are in very good agreement with IR TDLAS measurements achieved in Bell Jar reactor [2]. We can conclude that the methane is mainly converted into C_2H_2 , this species becoming the major carbon species in the chamber for high power density (from 100 mbar-2000 W).

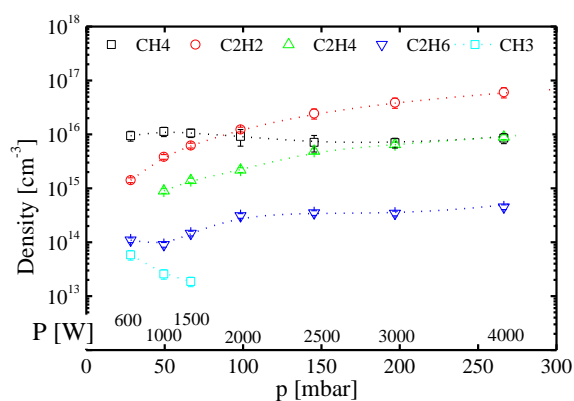


Fig.2 Carbon-containing species density according to pressure-power couple ($Z=1.6$ cm; 4% CH_4)

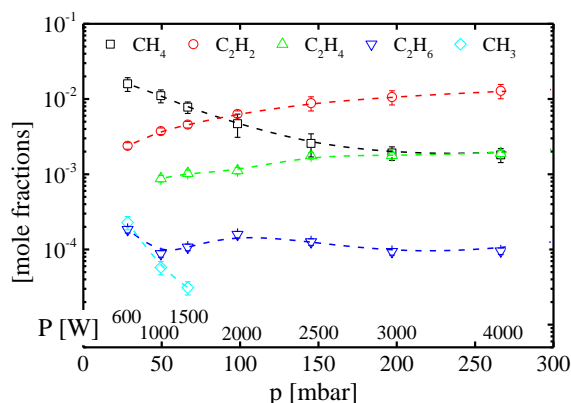


Fig.3 Carbon-containing species mole fraction according to pressure-power couple ($Z=1.6$ cm; 4% CH_4)

The relationship between methane and acetylene is also highlighted in Figure 4 that presents the species density according to the CH_4 content in the feed gas for a high pressure-power condition (270 mbar-4000W). Increasing the initial concentration of methane has no significant

influence in CH_4 and C_2H_6 densities but results in a strong increase in C_2H_2 density from $2.8 \times 10^{15} \text{ cm}^{-3}$ (1% CH_4) to $9 \times 10^{16} \text{ cm}^{-3}$ (7% CH_4). Consequently, we also notice a small increase of C_2H_4 .

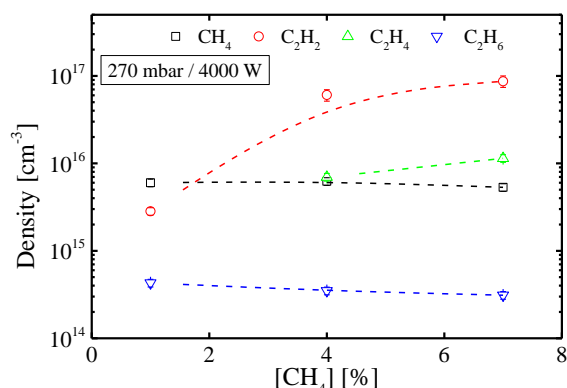


Fig.4 Carbon-containing species density according to methane content ($Z=1.6$ cm; 4% CH_4)

Mastering the initial methane content is essential because increasing the pressure and the power leads to the increase of hydrogen density [4]. In order to avoid etching process on diamond surface, the methane content has to be adjusted. However high methane concentration used with high pressure-power conditions lead to soot formation in the chamber that can damage the process. We note that C_2H_2 density becomes quite constant from 5% of methane. This evolution seems to be a consequence of soot appearance, acetylene being known as a small HC precursor for aromatic compounds.

5. H₂/CH₄/B₂H₆ PLASMA

Preliminary IR absorption measurements have been achieved in $H_2/CH_4/B_2H_6$ CVD plasma. The lines of B_2H_6 have been monitored in the range of 2600 cm^{-1} . However BH_3 lines at 2587.544 cm^{-1} (Q 3-1) and 2587.921 cm^{-1} (Q 2-1) have been unsuccessfully monitored, the bands being overlapped by B_2H_6 spectra. Unknowing the line strength of B_2H_6 , the integrated absorption coefficient of the lines has been measured according to the pressure by monitoring the feed gas in the reactor without the discharge.

The presence of the carbon containing species in the feed gas has strong effects on measurements. With methane addition, the concentration of diborane is below the limit of detection of about $5 \times 10^{11} \text{ cm}^{-3}$. The spectral range of the B_2H_6 absorption lines is overlapped by CH_4 lines which are stronger than those of diborane (methane content is much higher than those of diborane).

Figure 5 presents B_2H_6 density according to the pressure-power couples from 50 mbar-1000W to 300 mbar – 4000W for two mixtures (30 ppm or 66 ppm of B_2H_6 diluted in H_2). For low experimental conditions, the degree of dissociation of B_2H_6 decreases with pressure and power whereas from 100 mbar – 2000 W the degree of dissociation becomes constant and so the B_2H_6 density increases as the pressure.

Additional measurements on CH_4 , C_2H_2 , C_2H_4 and C_2H_6 absorption lines have been achieved in $H_2/CH_4/B_2H_6$ plasma. As presented in the previous part, parametric studies on carbon species densities changing either pressure-power couple (from 60 mbar 1000 W to 100 mbar 2000W) or methane content (from 0 to 5%) have been carried out. For these low pressure-power conditions, there is no significant influence of diborane on carbon species densities, the results are very close to those presented in the previous part.

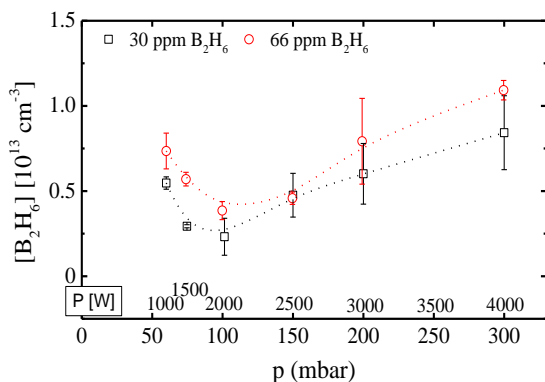


Fig5 Mole fraction of B2H6 vs Pressure/power

However the presence of B_2H_6 in the feed gas has strong effect on the discharge for high pressure-power conditions. Indeed addition of diborane into a stable plasma working at standard growth conditions (*e.g.* 200 mbar-3000 W, 5 % CH_4) involves immediately soot formation in the chamber. Operating conditions are limited for boron doped diamond elaboration.

CONCLUSION

IR-TDLAS measurements have been carried out in H_2/CH_4 and $H_2/CH_4/B_2H_6$ MW plasmas for determining the density of several carbon containing species and diborane. The results show an increase of the degree of dissociation of CH_4 and B_2H_6 with pressure and power. C_2H_2 is the most abundant reaction product. The concentration of CH_3 was detected to about 10^{13} cm^{-3} that corresponds only to low power density conditions. In the presence of methane,

the concentration of diborane decreased below the limit of detection of about $5 \cdot 10^{11} \text{ cm}^{-3}$ and soot particles appear at high power density, limiting the operating conditions for boron doped diamond growth.

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