Chemical kinetics of H_2/CH_4 plasmas for high pressure/high power growth conditions used in diamond MPACVD

N. Derkaoui[1], C. Rond[(*)], O. Brinza, M. Wartel, A. Gicquel

[1] *LSPM, CNRS-UPR3407, 99 avenue JB Clement , 93430 Villetaneuse,France*
[(*)] rond@lspm.cnrs.fr

Optical emission spectroscopy has been used to characterize diamond MPACVD plasmas operating at high power density. H-atom density in the plasma bulk and near the diamond substrate surface have been estimated using actinometry technique for a wide range of working conditions (pressure [25-400] hPa and MW power [600-4000] W). An increase of the pressure and power causes an increase of H atom mole fraction in the plasma bulk from 0.1 to up to 0.6 and the rise of the [H] near the surface up to $2.6.10^{16}$ cm^{-3}. Furthermore, we show that the growth rate can be seen as entirely governed by H atom production.

I. Introduction

Microwave plasma assisted chemical vapour deposition (MPACVD) for diamond growth have been widely studied under medium pressure conditions, for which H atoms and CH_3 radicals have been shown to constitute the key species for growing crystal diamond [1-4]. In particular Goodwin [1] has established a simple growth model which highlights the role of the surface concentrations of these both species. The growth of very high purity and high quality diamond at ultra-high rates relies on high production of hydrogen atoms and methyl radicals in a very clean system, and their transport to the growing surface. To understand how the experimental conditions impact the growth mechanisms at high pressure/high power (> 100 hPa, > 2 kW) H and CH_3 plasma concentrations have to be determined, especially near the surface. In this work, optical emission spectroscopy is used to provide experimental quantitative evidences on the mechanisms that drive the diamond growth at high power density and to compare them with theoretical model. The relationship between H-atom density and growth rate is discussed.

II. Experimental Results

The microwave (MW) diamond deposition reactor is a water-cooled stainless steel nearly resonant cavity that has operated at high pressure (up to 400 hPa) and high power density operations (1500-4000 W). The discharge, produced by a 2.45 GHz MW generator, sparks off the activation of the feed gas (0-7%CH_4/4%Ar/H_2) which leads to the formation of a close to hemispheric plasma on the 5 cm diameter substrate holder supporting a crystal diamond substrate. Actinometry technique, which has already been validated for diamond deposition in CVD reactor [5-7], is used for probing hydrogen atom for high power density conditions. Emission spectra of H_α (656.3 nm), H_β (486.1 nm), and 4p→4s Argon transition (2p1→ 1s2 at 750.3 nm) were recorded into the plasma bulk (1.5cm above the substrate) for different power density conditions. From these measurements we highlight that, as the pressure is increased from 25 hPa to 400 Pa and simultaneously the power from 600 W to 4000 W, the H-atom mole fraction rises from 0.1 to around 0.6 and also that the electron temperature decreases from 16000 K to around 11000 K.

Since diffusion is responsible for the H-atom transport to the surface, the surface H-atom mole fraction is linearly related to its maximum value into the plasma volume. Figure 1 shows that the higher the power density, the higher the [H] surface, reaching an asymptote at 2.10^{16} cm^{-3} for pressure higher than 250 hPa. Indeed, increasing the power density decreases the mass boundary layer and so rises the H atom flux to the surface. These results are compared with calculated one and spatially resolved H emission measurements that provide [H] surface mole fraction. Furthermore, H atom concentrations from actinometry technique are to be compared with H-TALIF measurements. Finally from modelling, we have demonstrated that CH_3 concentration at the surface is a linear function of the H-atom density into the plasma bulk and of the square root function of methane percentage introduced

in the discharge. Then from Goodwin model we can state that, at very high power density, the growth rate is entirely governed by H atom production leading to the following frame:

$$k(T_s)\frac{k'}{2}[H]_\infty < G_{100} < k(T_s)\,k'[H]_\infty \quad (1)$$

Figure 2 shows that equation (1) well describes experimental values of the growth rates measured in our laboratory.

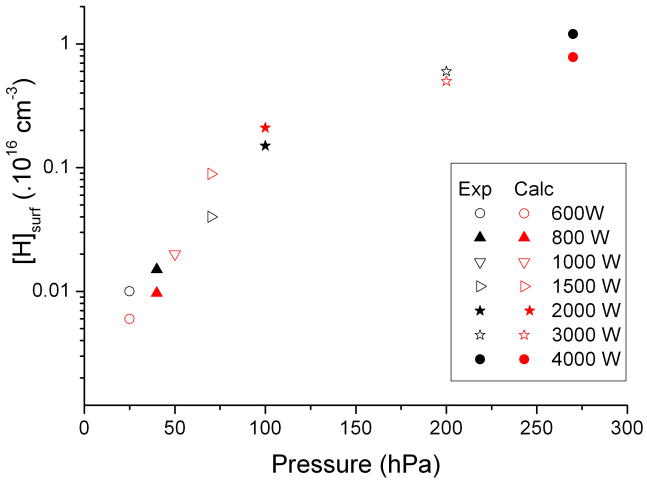

Fig. 1: H surface density vs pressure and microwave power

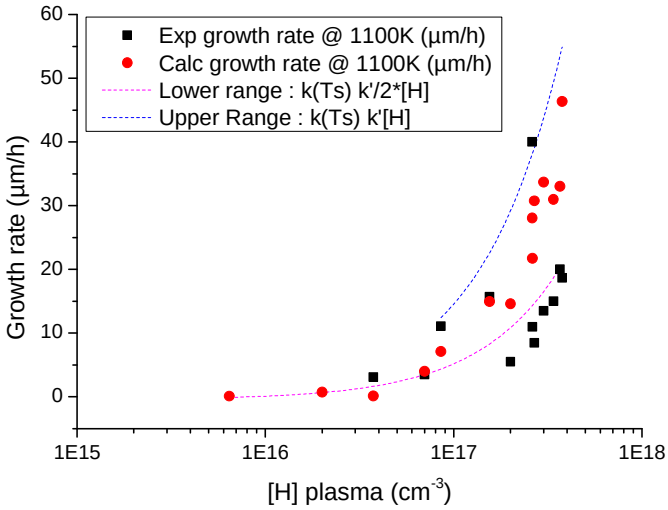

Fig 2. Growth rate vs $[H]_{plasma}$

References

[1] D. G. Goodwin, *J. Appl. Phys.* 74 (1993) 6888-6894
[2] D. G. Goodwin, *J. Appl. Phys.* 74 (1993) 6895-6906
[3] D. G. Goodwin and J. E. Butler, *G. P. M.A. Prelas, and L.K. Bigelow* (1997), NY, NY, 527-581
[4] J. E. Butler, Y. A. Mankelevich, A. Cheesman, J. Ma and M. N. R. Ashfold, *Journal of Physics: Condensed Matter* 21 (2009) 364201
[5] A. Gicquel, M. Chenevier, K. Hassouni, A. Tserepi and M. Dubus, *J. Appl. Phys.* 83 (1998) 7504-7521
[6] J. Ma, M. N. R. Ashfold and Y. A. Mankelevich, *J. Appl. Phys.* 105 (2009) 043302-12
[7] A. Gicquel, N. Derkaoui, C. Rond, F. Benedic, G. Cicala, D. Moneger and K. Hassouni, *Chemical Physics*, (2011) doi:10.1016/j.chemphys.2011.08.022