Self-consistent simulation of hydrogen-methane plasmas for growth of carbon materials

S. Prasanna[1], A. Michau[1], K. Hassouni[1]

[1] *Laboratoire des Sciences des Procédés et des Matériaux, UPR3407, CNRS, Universite Paris 13, avenue Jean-Baptiste Clément, 93430 Villetaneuse (France)*

MW assisted hydrogen methane plasmas have been extensively used for growth of CVD diamond and graphene. For the growth of carbon based materials, a mixture of hydrogen methane and other gases is the precursor gas operating at a pressure ranging from 20 mbar to 300 mbar. The quality of the deposit is strongly affected by parameters such as pressure, microwave power and the concentration of precursor gases. In this article, we discuss the results of self-consistent simulation of hydrogen-methane plasmas in a microwave resonating cavity over wide range of operating conditions (25-200mbar) and different concentrations of methane. The main focus of the paper is to highlight the effects of precursor gases on the plasma microwave interaction.

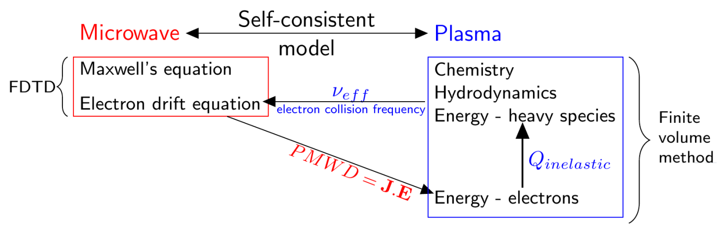

Figure 1: Schematic of the self-consistent model

The self consistent model has been described in detail elsewhere [1] and only a brief desciption would be provided here for the purpose of completion. The computational model consists of two modules namely the plasma module, which solves for chemistry and hydrodynamics and the MW module which solves the Maxwell's equations. One assumes a two temperature model where the heavy species is assumed to be at gas temperature T_g while the electrons are at electron temperature T_e. The MW module calculates the microwave power density injected inside the plasma for the species calculated by the plasma module. Thus the two modules are solved sequentially until the plasma characteriestics such as species concentration, T_g, T_e and microwave power density converges. Methane-hydrogen chemistry is very stiff especially at higher pressures. The numerical simulations are initially performed at low pressures and are gradually increased to higher pressures.

The results indicate that the pressure, power and concentration of methanne in the $H_2 - CH_4$ methane affect the characteristics of the coupling between MW and plasma. Figure 2 shows the contour map of electron concentration as a function of methane concentration in a bell jar reactor at 25 mbar and 750 W. The results clearly indicate addition of methane affects the plasma-

MW coupling. The bell jar reactor is characterized by a presence of two anti-nodes, one close to the substrate and the other on top of the bell jar. For high concentration of methane, a single ball plasma transforms to a two ball plasma. In other words, the plasma becomes unstable with the addition of methane.

The present observation can be explained by the dominant ions present in the reactor. In a pure hydrogen plasmas, the dominant ions under these conditions is H_3^+. However, with the addition of methane, the dominant ion species shifts to CH_5^+ and $C_2H_3^+$ depending on the concentration of methane. As the hydrocarbon ions are heavier compared to the hydrogen ions, the diffusion of hydrocarbon ions is much lower than the hydrogen ions. Consequently, higher ion density and thus electron density (due to electro-neutrality and ambi-polar diffusion prevailing under these conditions) is observed in the plasma core. This means the hydrocarbon plasmas observe higher power dissipation close to the substrate than the hydrogen plasmas.

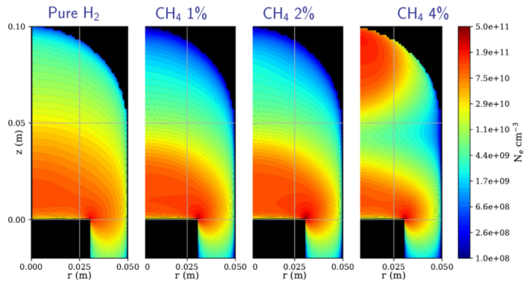

Figure 2: Effect of methane on the MW-plasma coupling at pressure 25 mbar and 750 W

The above observations are also true for higher pressures. Figure 3 shows the atomic hydrogen concentration and microwave power density at a pressure of 110 mbar and power 1250 W. Unlike the low pressure conditions, the microwave density is not seen to be much affected by the addition of hydrocarbons. There are however small changes to the sizes of the plasma where the size of hydrocarbon plasma becomes larger than that of pure hydrogen plasmas. The temperature of the plasma is around 2500 K and increases with increase

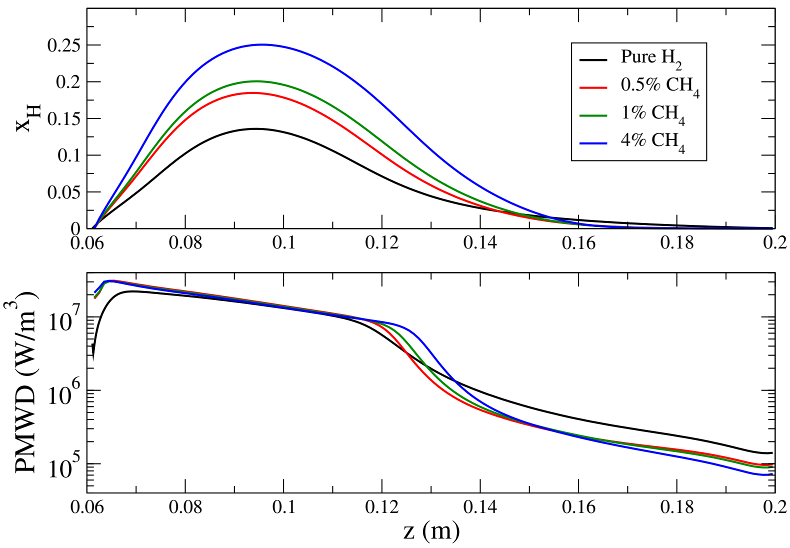

Figure 3: Effect of methane on the atomic hydrogen mole fraction and microwave power density PMWD at 110 mbar and 1250 W at the axis of the plasma reactor

in methane concentration. The increase in temperature is majorly due to low diffusion and lower thermal conductivity of hydrocarbon plasma over hydrogen plasmas. Moreover, the conditions of the plasma dictates dissociation of hydrogen molecule through thermalization. Thus the increase in gas temperature of the plasma in turn causes substantial increase in the concentration of hydrogen concentration with addition of methane. These results are also consistent at 200 mbar. These results are very important from the point of view of CVD diamond growth as hydrogen is known to etch the graphitic carbon formed.

References

[1] S. Prasanna et al. Plasma Sources Science and Technology **26.9 (2017)**