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Quantitative analysis of diamond deposition reactor efficiency

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ABSTRACT

Optical emission spectroscopy has been used to characterize diamond deposition microwave chemical vapour deposition (MWCVD) plasmas operating at high power density. Electron temperature has been deduced from H atom emission lines while H-atom mole fraction variations 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 from 14 hPa to 400 hPa with a simultaneous increase in power causes an electron temperature decrease from 17,000 K to 10,000 K and a H atom mole fraction increase from 0.1 to up to 0.6. This last value however must be considered as an upper estimate due to some assumptions made as well as experimental uncertainties.

1. Introduction

At long term, single crystal diamond films with very high purity is believed to outperform silicon in devices such as switches working at voltages of 10 and up to 20 kV. Some key bottlenecks must however be over-passed to reach this era. They concern mostly today the ability to synthesize very high quality bi-polar (intrinsic, n-doped, p-doped and p+ doped) or even uni-polar (intrinsic, p-doped and p+ doped) multilayers all in diamond, to reduce substantially the dislocation density inside the crystals (typically of $10^4/cm^2$ for the state of the art), to enlarge the diamond single crystal layers and to grow 100 μm to 1 mm thick films at very high growth rates. Part of these issues, in particular the last one, is based on the capability to produce very energetic and very high purity plasma able to run for long deposition time (for thick films). The goal is to produce a large amount of atomic hydrogen in the plasma that diffuses towards the substrate as well as CH_3 radicals at the plasma/surface interface, these species being key for diamond deposition.

Microwave plasma reactors, running at pressure typically in the range of 100–400 hPa with some kilowatts power coupled to the plasma, answer pretty well to this purpose. These reactors have been extensively studied for conditions of moderate power density (less than 30 W cm^{-3}), in particular by Gicquel's group in collaboration with different laboratories [1–12], but also by Ashfold and Mankelevich [13–20], as well as Grotjohn et al. [21–23]. However the conditions of very high power density (high pressure and high microwave power coupled to the plasma) have not been studied so much. In particular, even if some works have been carried out [6,18], there is still lacks in experimental validations of the simulation codes and basic studies aiming to determine the main parameters (species, flow,...) responsible for doping as well as for soot formation which has been observed under conditions of high power density coupled to high methane input, and more recently in presence of diborane in the plasma.

In the past, different spectroscopic methods have been employed to monitor the gas phase chemistry and composition in diamond deposition reactors. In particular, absorption spectroscopy and laser induced fluorescence (LIF) spectroscopy have been used due to their capability in accessing ground state species. Thus, ground state H atoms, which is a key factor for CVD diamond deposition, has been studied in microwave plasma reactors at low to moderate power density by Two-photon laser induced fluorescence (TALIF) [2–4] to estimate the temperature and relative mole fraction of H atoms, while ground state molecular hydrogen temperature have been measured through coherent anti-stokes Raman spectroscopy (CARS) spectroscopy [1,2,24].

Concerning carbon containing species, the ultraviolet absorption of CH_3 at 216 nm was used for number density measurements firstly in hot filament reactors and later on in plasma reactors. Most recent experimental advances derive from the improvement of laser absorption spectroscopy methods that have allowed accessing to stable hydrocarbon species like CH_4, C_2H_2 as well as transient species such as CH_3 radicals through IR absorption using tunable diode laser [8,12,25–27] and quantum cascade laser (QCL) [19,28]. Furthermore, CH_3 radicals have also been monitored in microwave reactors using cavity ring-down spectroscopy (CRDS) [20]. Finally, laser induced fluorescence (LIF) observations of CH and C_2 radicals

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have been also reported in dc-arcjet plasma for diamond deposition providing gas temperature [29,30] and absolute concentration of C_2 [31].

These diagnostics are powerful methods for probing species on their ground electronic states. However the nonflexible and expensive characteristics of these advanced techniques make them unfit for diagnosing industrial reactors, and then comparison between different MW reactors seems hard to be considered.

Optical emission spectroscopy (OES) measurements on radiative species can be a powerful technique for accessing plasma characteristics, provided it is coupled with a very detailed analysis of all the electronic excitation processes to obtain ground state density information. Actinometry technique has been demonstrated to be valid in diamond CVD reactor for probing hydrogen atom [4] and then was used to determine the spatially resolved H relative density for low to medium pressure conditions (100 hPa > p > 25 hPa, 2000 W > P > 600 W). Lang et al. also reported results at low pressure conditions (50–100 hPa; 400–880 W) [32], and recently Ma et al. [13] proposed a spatially resolved studies of H relative density for higher pressure conditions (<200 hPa; 1.5 kW).

Increasing power and pressure (i.e. power density) enhances drastically CVD diamond growth rates [33,34] and quality [35–37]. Indeed, increasing the MW power density results in a lower electronic temperature but in a higher gas temperature [6,9]. As at high power density (>15 Wcm^{-3}, i.e. p > 50 hPa, P > 1000 W), the main H-atom production channel is thermal dissociation [9], as a result: the higher the MW power density, the higher the H density and the more efficient the diamond CVD process.

Previous works referred above have been carried out for moderate power density conditions. This paper focused on the study of the plasma phase for high power density growing conditions using actinometry method. Another goal is to analyze the validity of this technique for H atom at high pressure/power conditions by comparing experimental and simulated results. Variations of both electron temperature and H-atom density as a function of the power density, monitored by the couple (pressure, microwave power coupled to the plasma) will be discussed. This paper constitutes a first part of a larger program aiming to put forward our knowledge of diamond deposition reactor operation, when running at high power density.

2. Experimental set-up and diagnostics

2.1. Microwave reactor

The microwave diamond deposition reactor, which was described elsewhere [35], is a water-cooled stainless steel resonant cavity that operates at moderate pressure and dedicated to high power density operations (Fig. 1). The discharge is generated by a 2.45 GHz MW generator delivering a maximum power of 6 kW along a rectangular waveguide up to a cylindrical chamber. At the centre of this chamber, a 5 cm in diameter substrate holder is supporting a either polycrystalline or single crystal diamond substrate. Both are immersed in a close to hemispheric plasma emerging from MW activation of the feed gas. The gas consists in a mixture of CH_4 (0–4%) and Ar (3–4%) diluted in hydrogen and supplied by a total flow rate range of 100–500 sccm. Substrate temperature, monitored using a monochromatic IR pyrometer, can be varied from 620 °C to 915 °C, independently from the plasma conditions. For this specific study, it was maintained at 850 °C. The total pressure in the reactor chamber was adjusted in order to keep as much as possible constant the plasma volume (the dimension of which reminding anyway difficult to estimate). The goal of this procedure is to maintain the ratio of the power coupled to the plasma over the total density constant. However, we cannot report the estimation of the input power fraction really coupled to the plasma relatively to the plug-in power that is lower due to the Joule effect energy loss. This has been made in a bell jar reactor operating at low power density evidencing that more than 90% of power was coupled to the plasma [56]. Under conditions of high power density this is obviously not the case as evidenced by the observed strong heating of the microwave guides and quartz windows. This necessarily leads to errors in defining the average power density, expressed in W cm^{-3}. As a consequence, the experimental conditions of (pressure-MP power) couple will be most of the time specified rather than the power density.

In the frame of this study, large ranges of pressure (25–400 hPa) and MW power (600–4000 W) were used, focusing our attention on high power density conditions. It is worth noting that the results obtained previously at low pressure and power in a bell jar reactor are reported in this paper. The link between these sets of experimental results is provided through calibrations.

2.2. OES measurements

A scheme of the MW reactor and the OES set-up is shown in Fig. 1. The steel cavity contains three optical fused silica windows. An Acton 2500i spectrometer equipped with an ICCD camera was used to perform emission spectroscopy. Most of the measurements have been carried out using a 1800 g/mm grating blazed at 500 nm, except for H_β (n = 4) spectra obtained with a 2400 g/mm holographic visible grating.

The light emitted from the plasma was collected by an afocal lens system and transported via a 1 mm optical fibre core to the entrance slit (10 μm) of the monochromator. This device 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 and radial measurements. Emission intensity, averaged on a line of sight, is measured at 90° to the axis of the reactor. At a given location in the plasma, as the plasma volume is kept as much as possible constant, the line-of-sight averaged emission intensities are always measured within approximately the same plasma volume.

Spectra of H_α (λ = 656.5 nm), H_β (λ = 486.1 nm), and 4p → 4s argon transition (transition 2p1 → 1s2 at λ = 750.3 nm) were recorded systematically (Fig. 2a). Table 1 gives the different transitions used.

2.2.1. Actinometry method

Actinometry was introduced in the early 80's [38] in order to estimate relative densities of a ground state species from OES measurements. The principle and the validation of the method applied to H-atom relative density measurements has been thoroughly described previously [1,4] and then by Ma et al. [13].

Briefly, actinometry requires the introduction of a small amount of an inert gas (here argon) to the mixture, which constitutes the actinometer. The emission intensity ratio (probed species over actinometer) is proportional to the species electronic ground state relative concentration, provided that (i) the two species are excited from their electronic ground state by a single electron impact; (ii) the excitation cross section of these processes are similar (same energy threshold, proportional for the considered electron energy range); (iii) radiative de-excitation processes are predominant. Quenching processes have to be taken into account for high pressure conditions.

Argon has been chosen as actinometer to study the relative density of H atom in diamond CVD plasma, since its excited state (4p) is produced by direct electron impact processes from the 3p6 ground state under the conditions studied here, the excitation cross section of which being similar in shape as that of H(n = 3). The main processes involved in the production and loss of H(n = 3) and Ar(4p) (sublevel $2p_1$) have been widely studied and presented in [4]. As well