DETERMINATION OF ABSOLUTE ATOMIC HYDROGEN DENSITIES BY TWO-PHOTON ABSORPTION LASER INDUCED FLUORESCENCE IN A H_2/CH_4 MICROWAVE PLASMA AT HIGH PRESSURE AND HIGH MICROWAVE POWER

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ABSTRACT

In the context of monocrystalline diamond plasma deposition, the atomic hydrogen densities have been determined by two-photon absorption laser induced fluorescence in a H_2/CH_4 microwave plasma at high pressure ($\geq$ 200 hPa) and high microwave power (3000 W). H-atom densities were estimated by a calibration method that consists in normalizing the H-atom TALIF intensity by the intensity from Kr atoms in a pure krypton gas at a known pressure. In the range of pressures studied, the value of the H-atom fluorescence yield, which is necessary for the calculation of absolute densities, cannot be determined experimentally, but is estimated from a model calculation that solves the rate equations describing the population changes in the various H $n=3$ sublevels. In plasmas containing 1% CH_4, the H-atom densities reach values $\geq 1.9 \times 10^{23}$ m^{-3}, and the gas temperature in the plasma bulk is ~3000 K.

1. INTRODUCTION

The use of single crystal diamond films for the design of electronic component represents one of the most attractive pathways for the replacement of current silicon based electronic devices. Diamond is a wide band-gap semiconductor exhibiting a fast switching capability, a high breakdown voltage, and a low leakage current associated with a high thermal conductivity, properties which are appropriate for high power electronic devices. The fabrication of these devices relies on the ability to synthesize thick layers (>100 μm) of intrinsic and p-doped mono-crystalline diamond, with a high microstructural quality (low dislocations and impurities levels) at high growth rates (~ 10 μm/h). The growth of thick diamond films is achieved by Microwave Plasma Assisted Chemical Vapour Deposition in H_2/CH_4 chemistry operating at high pressure ($\geq$ 200 hPa) and high microwave (MW) power ($\geq$ 3000 W). The MW H_2/CH_4 plasma produces a large amount of hydrogen atoms in the plasma core that diffuse towards the substrate, whereas CH3 radicals are produced in areas where the gas temperature is close to 1650 K, i.e. the surrounding plasma ball and the plasma/surface interface; both H and CH_3 radicals are key species for diamond deposition [1]. In such conditions, an accurate description of the plasma gas phase interacting with the surface of the growing crystal is needed to optimize the plasma deposition process and control the film properties.

This study focuses on the determination of absolute atomic hydrogen densities by the use of laser diagnostics, completing a previous study using Optical Emission Spectroscopy (OES) [2]. The Two-Photon Absorption Laser Induced Fluorescence (TALIF) technique has been implemented to determine axial profiles of H-atom densities in the H_2/CH_4 microwave plasma. Compared to a line-of-sight technique like OES, the TALIF technique provides an excellent spatial resolution, and probes directly the electronic ground state of H atoms.

2. EXPERIMENTAL SET-UP

The microwave reactor for diamond film deposition is a water-cooled stainless steel nearly resonant cavity operating at high pressure (25 – 400 hPa) and high MW power (600 – 4000 W). The discharge, produced by a 2.45 GHz microwave generator, sparks off the activation of

the gas mixture (0 – 10% CH_4 / H_2) leading to the formation of an approximate hemispheric plasma on the 6 cm diameter substrate holder supporting a crystal diamond substrate. The stainless steel reactor is equipped with 4 optical windows to support spectroscopic experiments in a wide wavelength range and allow both axial and radial profile measurements.

The experimental device used for TALIF experiments is presented on figure 1. The detection of H atoms is carried out following the excitation/emission scheme first proposed by Bokor et al [3]. In this scheme, electronic excitation from the H 1s ground state to the 3s $^2S_{1/2}$ and 3d $^2D_{3/2,5/2}$ excited states is obtained by two-photon absorption at 205.1 nm, according to the two photon selection rules ($\Delta L=0,\pm 2$, $\Delta S=0$ and $\Delta J=0,\pm 1,\pm 2$).

A dye laser pumped by a Nd:YAG laser is used for photon flux generation at 205 nm. The frequency doubled emission at 532 nm of the YAG laser pumps a Rhodamine (610/640) mixture to generate an intense laser beam (~60 mJ/pulse) close to 615 nm. Two harmonic generator units then operate a frequency conversion to obtain a laser beam (~5mJ/pulse) at 205 nm. The laser beam in the UV region is sent and focused within the reactor by a set of two UV grade silica prisms and a plano-convex lens (f = 350 mm). The energy adjustment of the laser beam is ensured by a Glan polariser. Two beamsplitters, located at the entrance and the exit of the plasma reactor respectively, deflect a minor part of the laser beam to joulemeters for monitoring the laser energy and measuring the absorption of the laser beam through the plasma chamber. After excitation to the H n=3 excited level, fluorescence emission (n=3 → n=2) from the Balmer-α lines at 656.3 nm (cf. figure 2) is collected by a set of two lenses (f = 500 mm and f = 100 mm) and detected by a photomultiplier tube after passing through an interferential filter (656.2 nm, FWHM 10 nm) and a slit of height 200 μm and of width 500 μm. Both optical systems for laser excitation and fluorescence collection are mounted on motorized translation plates, providing axial and radial profiles of H fluorescence signal.
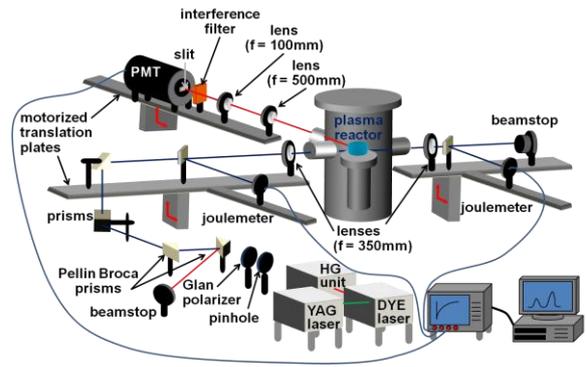
Fig. 1TALIFexperimenal device

3. DENSITY CALIBRATION

The fluorescence signal intensities recorded in TALIF experiments are directly proportional to the ground state density of H atoms. However, several parameters which are necessary to calculate the absolute H-atom densities cannot be determined precisely, thus TALIF measurements remain qualitative in practice. To access absolute H-atom densities, a calibration method is needed. The method that is implemented in this study consists in normalizing the H TALIF intensity by the TALIF intensity from Kr atoms in a pure krypton gas at a known pressure. Kr atom exhibits an excitation/emission scheme similar to H atom (cf. Figure 2), which gives the advantage of using the same laser device and ensures the same spectral, spatial and temporal intensity distribution of the laser radiation for both TALIF excitations. Considering a quadratic regime for H and Kr atoms, the ratio of time integrated fluorescence signals S_X can be expressed from the equation:

$$\frac{S_H}{S_{Kr}} = \frac{T_H}{T_{Kr}} \frac{\sigma_H^{(2)}}{\sigma_{Kr}^{(2)}} \frac{g(\Delta \upsilon)_H}{g(\Delta \upsilon)_{Kr}} \left(\frac{I_H \nu_{Kr}}{I_{Kr} \nu_H} \right)^2 \frac{q_{fH}}{q_{fKr}} \frac{n_H}{n_{Kr}} \quad (1)$$

where T_X is the optical sensitivity of the detection device, $\sigma_X^{(2)}$ the two-photon excitation cross section (m^4), I_X the laser pulse energy (J) at the ν_X frequency, n_x the atom density (m^{-3}) and $g(\Delta v)_X$ the spectral overlap fraction (s) between the laser spectral profile and the 2-photon absorption profile, normalised to 1. The parameter q_{fX} is the fluorescence yield, which represents the ratio of excited atoms that fluoresce to the total number of excited atoms.

Most parameters in equation (1) can be evaluated from spectroscopic constants or measured experimentally to retrieve the H-atom absolute densities. In the case of Kr atom, where a single level is excited through 2-photon absorption, the fluorescence yield is:

$$q_{fKr} = \frac{A_{5p \to 5s}}{A_{5p} + Q} = A_{5p \to 5s} \times \tau_{Kr} \qquad (2)$$

with $A_{5p \to 5s}$ the spontaneous emission coefficient (s^{-1}) of the fluorescence line observed, A_{5p} the total spontaneous emission rate (s^{-1}) from the excited level 5p and Q the collisional quenching rate (s^{-1}), which depends on the density of collision partners. At the end of the laser excitation, the fluorescence signal from excited Kr level 5p decays exponentially with an effective fluorescence lifetime τ_{Kr} that can be determined experimentally. Figure 3 presents the effective fluorescence lifetime of Kr atoms measured for two emission lines from the Kr 5p level, at 826.3 nm and 587.1 nm, and a comparison with theoretical values [4]. Though much less intense, the 587.1 nm line is better suited because it does not suffer from disturbance phenomena such as self-absorption or amplified spontaneous emission (for laser energies up to 150 μJ, with a beam diameter ~1 mm). The choice of the Kr fluorescence emitting line is therefore crucial for a correct absolute calibration of the H-atom densities.

In the case of TALIF measurements on H atoms, the absorption of two UV laser photons leads to the electronic excitation of 3s and 3d sublevels. In the range of H$_2$/CH$_4$ plasma pressures investigated (200 – 400 hPa), collisions with H$_2$ molecules, H atoms and other plasma species induce both a redistribution of the population within the $n=3$ sublevels (3s, 3d and 3p) and quenching out of these sublevels.
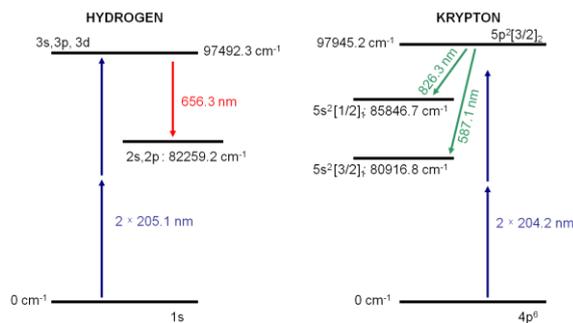
Fig. 2 Excitation/emission schemes used for TALIF experiments
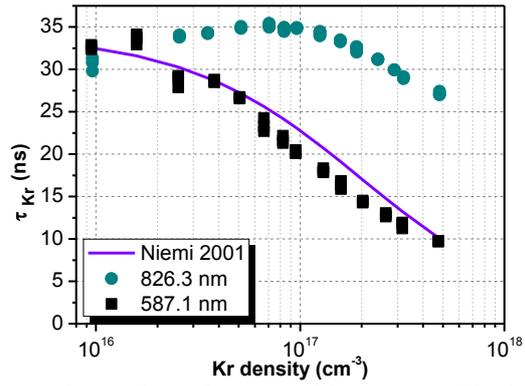
Fig. 3 Effective fluorescence lifetime measured for the Kr emission lines at 826 nm and at 587 nm and compared to theoretical lifetime [6]

The fluorescence yield q_{fH} is then a complex function of the population densities of the $n=3$ sublevels, the collision partner densities, and the rate constants for quenching and mixing, that depend on the temperature.

5. RESULTS AND DISCUSSION

TALIF measurements on H atoms were carried out for axial distances from the substrate in the range 0.5 – 32 mm. The TALIF calibration with Kr gas was carried out at the axial distance 15 mm, which corresponds to the plasma bulk. Figure 4 displays the calculated H-atom densities times the H fluorescence yield q_{fH} for various pressures in the 200 – 400 hPa range at a fixed power of 3000 W and 1 % CH$_4$. The fluorescence yield q_{fH} is expected to vary strongly as a function of the axial distance, since MW H$_2$ and H$_2$/CH$_4$ plasmas show high spatial gradients in temperature and densities of species [2, 5]. This behaviour is illustrated in figure 4, where spatial gradients in (relative) H-atom densities become steeper as the pressure increases, in particular at the plasma – surface interface.

In the plasma bulk, the H temperature, assimilated to the gas temperature [6], is ~3000 K from a measurement of the Doppler broadening of the H absorption line. According to this value, the fluorescence yield q_{fH} in the plasma core was estimated from a model calculation that solves the rate equations describing the population changes in the various H $n=3$ sublevels. The model uses collisional mixing cross sections from Glass-Maujean *et al* [7], and quenching cross sections calculated with the collisional diameters of the ground electronic
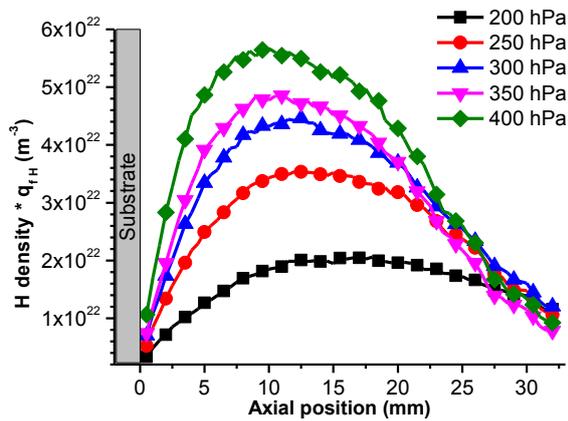
Fig. 4 H-atom density × H fluorescence yield versus axial distance from the substrate for various pressures (99% H_2 / 1% CH_4 plasma, 3000 W, 500 sccm, 200-400 hPa)

states (13×10^{-20} m^2 and 19×10^{-20} m^2 for $\sigma_{H/H}$ and $\sigma_{H/H2}$ respectively) rather than previously reported values at lower pressure [8, 9]. As the pressure increases from 150 to 400 hPa, the fluorescence yield is seen to decrease from 0.064 to 0.034 in the plasma bulk. While the calculated absolute H-atom densities are reasonable at 150 hPa (1.9×10^{23} m^{-3} in the plasma core, which corresponds to a H-atom molar fraction of 0.5), the values obtained at pressures greater than 200 hPa are high, corresponding to a complete dissociation of the H_2 molecules in the MW plasma. The uncertainties associated with the ratio of the 2-photon excitation cross sections for Kr and H [4], the collisional mixing rate constants (the values published in [7] refer to collisions with H_2 molecules only, at room temperature) and the quenching rate constants (the values reported in [8, 9] were obtained for lower pressure and/or lower temperatures) could explain the high values calculated in this study. Spatially-resolved measurements of the gas temperature and TALIF measurements over a wider range of pressures are currently underway to refine the model parameters used in the calculation of the fluorescence yield q_{fH}.

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