Molecular gases dissociation in microwave plasmas via electronically excited states production of atomic species

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Abstract: The present paper will discuss about the plasma characteristics of two different low-pressure high-density microwave (MW) assisted plasma sources measured using laser spectroscopy (nanosecond Two photon Absorption Laser Induced Fluorescence – TALIF). In particular, hydrogen density of the plasma generated by coaxial and Electron Cyclotron Resonance (ECR) sources (operating range of 1-100 Pa) has been characterised by the use of a ns-pulsed TALIF setup.

Keywords: Microwave, Nitrogen, Hydrogen, TALIF, Atomic density.

1. Introduction

Production of atomic species such as hydrogen and nitrogen is a key to several applications. For example, atomic hydrogen plays an important role in plasma chemistry for its strong reducing and etching properties [1,2]. Similarly, atomic nitrogen finds application in medicine [3], manufacturing of microelectronics components [4] as well as plasma assisted combustion [5].

There can be several production channels of atomic species. For example, an effective pathway of molecular dissociation could be through electron impact reactions operating under high reduced electric field [2,6]. Other pathways could be through vibrational excitation of molecules leading to dissociative attachment. Thus, the dissociation of molecular species such as H_2 or N_2 varies with pressure and the discharge conditions.

Microwave assisted plasma sources such as ECR or coaxial can sustain plasma with high reduced electric field (up to 300-400 Td) and have high potential to produce significant dissociation. The aim of the study is to determine the dissociation of atomic species particularly hydrogen for two different new generation MW plasma sources namely (I) magnetized ECR sources working in the range 1-10 Pa and (II) a coaxial source working from 10 to 100 Pa using ns-Two-photon Absorption Laser Induced Fluorescence (TALIF) [7].

2. Experimental setup

Atomic hydrogen and nitrogen density can be effectively determined by setting up Two-photon Absorption Laser Induced Fluorescence (TALIF) experiments. This technique has been chosen as it has several advantages over absorption or passive spectroscopic techniques, as effectively explained in [8]. It is not limited by line-of-sight measurements and can rely also on high time resolution. Moreover, the possibility to avoid photon production in VUV region (10-200 nm, wavelength range where non-target species in the plasma would be excited as well, causing significant inaccuracies in performing measurements) is the main advantage of this technique compared to single photon LIF technique. TALIF has proved to be an effective diagnostic method to detect fluorescence emission of H, C, N and O atoms [9,10] by using tuneable lasers.

Fig. 1 displays the experimental setup used to perform the present study.

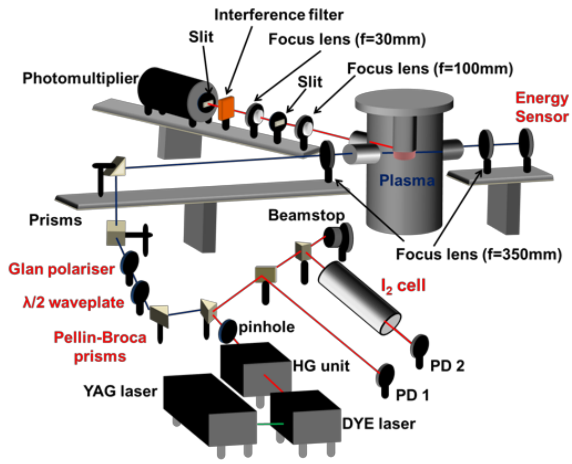

Fig. 1. Experimental arrangement deployed to perform TALIF measurements.

A Nd:YAG laser's (Quanta-Ray *Lab-Series* by Spectra-Physics) second harmonic (532 nm) has been used to pump a dye laser (Sirah dye laser system), based on a mixture of Rhodamine 610 and 640, that allowed the operator in detecting H (λ_{exc} = 205.1 nm) and N (λ_{exc} = 206.7 nm), with Kr as a calibration species (λ_{exc} = 204.2 nm). Fig. 2. shows the energy levels of H, N and Kr that are used to perform the quantitative TALIF measurement. Density of atomic hydrogen has been calculated by applying Equation 1:

$$n_H = \frac{\int_\nu \frac{S_H(\nu)}{E_H^2(\nu)} d\nu}{\int_\nu \frac{S_{Kr}(\nu)}{E_{Kr}^2(\nu)} d\nu} \frac{T_{Kr}}{T_H} \frac{\eta_{Kr}}{\eta_H} \frac{\sigma_{Kr}^{(2)}}{\sigma_H^{(2)}} \frac{\nu_H^2}{\nu_{Kr}^2} \frac{A_{Kr}}{A_H} \frac{\tau_{fluo\,Kr}}{\tau_{fluo\,H}} n_{Kr} \quad (1)$$

which shows the expression of the coefficient that correlates the densities of the target species (H) and the reference one (Kr). This magnitude is given by the ratio of several parameters, *i.e.* the integrals of the signal in the range where it linearly increases as a function of the squared laser energy; the transmissions T of the used filters at the fluorescence wavelengths for the two species; detector's quantum efficiency η at same wavelengths; two-photon excitation cross section $\sigma^{(2)}$; the frequencies of laser excitation of the two species in object; Einstein spontaneous emission coefficients A for the examined transitions (*i.e.* 5p-5s in Kr and 3-2 in H); decay time τ of excited state population.

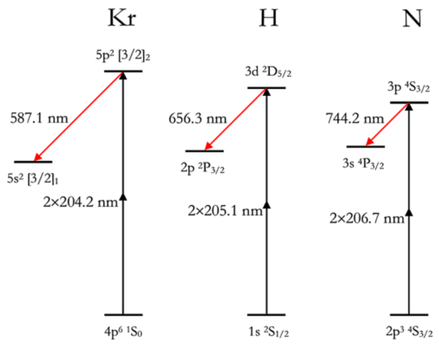

Fig. 2. Two-photons energy transitions schemes to perform TALIF measurements of H, N and Kr ground states.

3. Results and discussion

Measurements of H atom have been performed for wide range of pressure and power for the two plasma sources with pure hydrogen at different spatial locations.

Fig. 3 shows the comparison between ECR and coaxial sources operating at same pressure of 40 Pa for wide range of power conditions. The dissociation of hydrogen for ECR is not affected by the input power while the coaxial source shows strong coupling with MW power where the dissociation is most effective at 125 W after which hydrogen generated decreased. Also, the hydrogen dissociation with coaxial is much higher than the ECR power source. The possible explanation for this observation is that the ECR is more effective at lower pressures (1-10 Pa). However, it was not possible to perform the diagnostics at lower pressure owing to the very low signal to noise ratio making the observations unreliable. Efforts are being made to improve the acquisition at such low pressure conditions.

Fig. 4 shows the hydrogen density measured using coaxial source at two different pressure conditions. The dissociation seems to increase with pressure at lower power conditions. However, there is no difference in the hydrogen density between the two pressure conditions above 125 W. This is indicative of a strong coupling between MW and plasma for the coaxial source.

This configuration, though, has proved to be not effective for measuring atomic nitrogen densities, because of very high background emission. It is known that nitrogen can be estimated in the post discharge conditions. Thus, new experiments are being designed to pulse the plasma source and detect N(3p $^4S_{3/2}$) level emission in temporal post-discharge conditions.

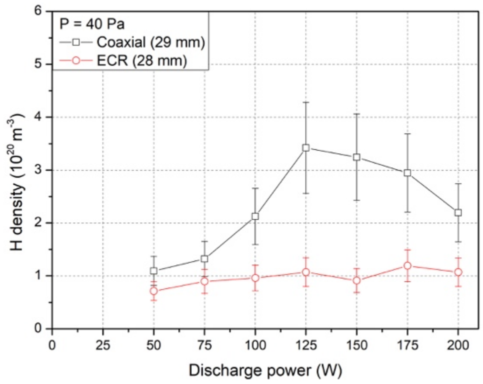

Fig. 3. A comparison between sources effectiveness operating at same conditions

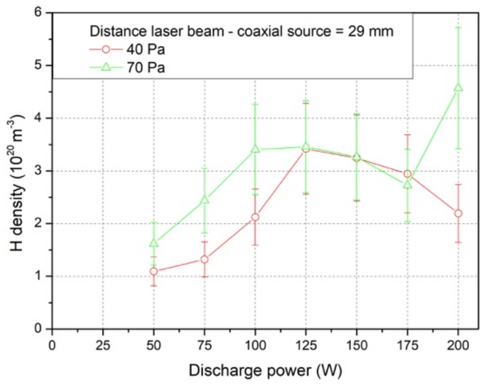

Fig. 4. Atomic Hydrogen density as a function of discharge power evaluating pressure effect at a fixed distance (29 mm) from coaxial source.

4. Conclusion

Hydrogen atom density has been determined via ns TALIF in low pressure (1-100 Pa) conditions, using a coaxial and an ECR MW plasma source. The coaxial source showed strong MW-plasma coupling. Furthermore, more diagnostics are being performed over a wide range of operating conditions which will be presented.

5. Acknowledgments

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