

Kinetics of H atoms in pulsed CH₄ – H₂ plasmas.

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Pulsed CH₄-H₂ plasmas are characterized by time resolved optical emission spectroscopy and electrostatic probe measurements. In the time post-discharge, decrease characteristic times below 1 ms are found for H atom densities. Influence of ion bombardment on the H loss rate at the chamber walls is discussed.

CH₄-H₂ based plasmas are widely used for dry etching of II-VI and III-V semiconductors. Pulsed plasmas combined to time resolved measurements are known to be powerful tools to study species kinetics [1, 2, 3]. This contribution is focused on the characterization of a CH₄-H₂ based pulsed ICP plasma, using time resolved electrostatic probes and optical emission spectroscopy (TR-OES).

Plasma conditions are: 800 or 1000 W RF power, 20 mTorr pressure. Period and duty cycle vary respectively from 5 to 50 ms and from 50 to 10 %. A cylindrical Langmuir probe (Smart Probe, Scientific System) and a home-made planar probe are used to measure electron density (n_e), electron temperature (T_e) and ion flux density. The species kinetics are investigated by TR-OES, with a iHR550 spectrometer (Jobin Yvon). As no emission occurs during the afterglow because T_e collapses when the excitation is cut off, we use the double pulse technique suggested by Bouchoule and Ranson [1] (see Fig. 1a.) and improved by Rousseau *et al.* [2]. The length of the probing pulse is 0.75 ms. This contribution is focused on the kinetics of H atoms. We use the H α line, and for relative quantification, we use pseudo-actinometry based on the Ar^{*} line ($2p_1 \rightarrow 1s_2$ at 750.4 nm).

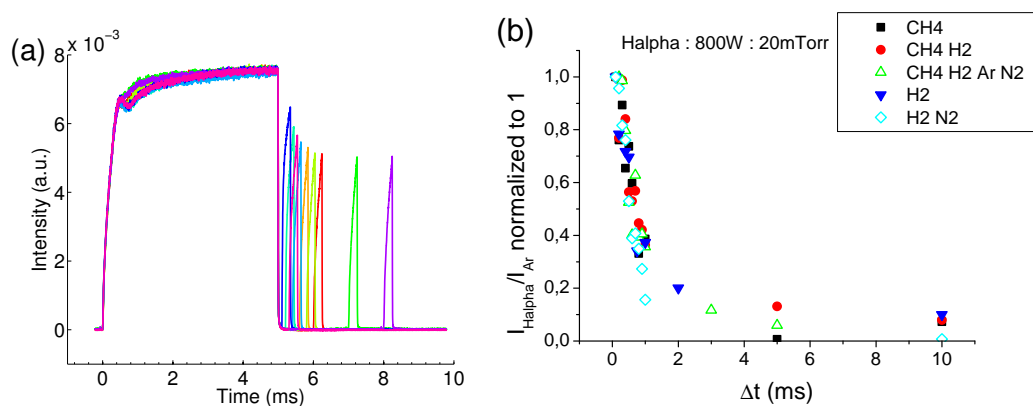


Fig. 1: (a) Stack of raw data obtained with the double pulse technique. (b) Time variations of H α to Ar^{*} line intensity ratio in the post-discharge.

The time evolution of n_e over one period reveals that n_e needs 1 ms to reach a stationary state and decreases with a characteristic time of about 0.1 ms (Fig. 2a.). T_e is not shown on Fig. 2a.; its measurement is difficult, especially in the post-discharge since the collected current is very low. However, the decrease time of T_e seems to be shorter than 0.1 ms.

Fig. 1b. shows the time variation of the H α to Ar^{*} line intensity ratio in the post-discharge for different gas mixtures. Although the H atoms kinetics are very fast, and characterized by decrease times below 1 ms (Table 1), they are slower than the time evolution of n_e and T_e . However, considering the diffusion coefficient of H atoms in the various gas mixtures, different rise and decrease characteristic

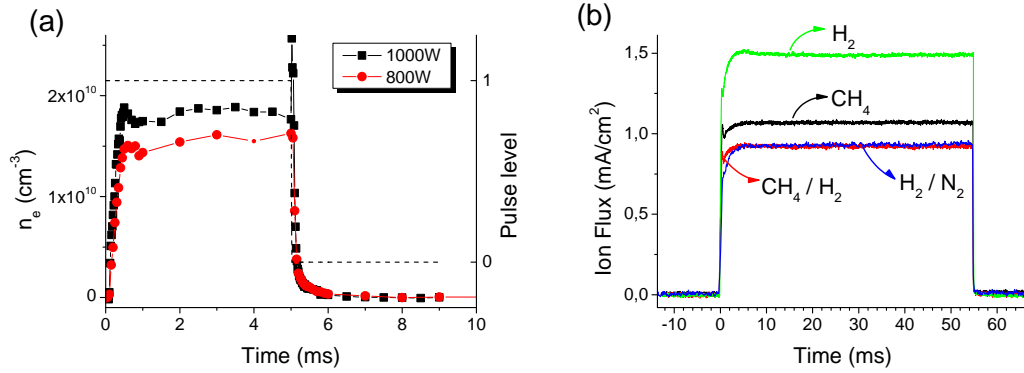


Fig. 2: (a) Time evolution of n_e for two different peak powers (50Hz 50%). (b) Time variation of ion flux for different gas mixture (2Hz 10%).

times could indicate different reaction probabilities on the walls, in relation with the gas mixture. Characteristic times and associated reaction probabilities, using Chantry's formalism [4], are listed in the Table 1. The H_α loss probability in the post-discharge (γ_{OFF}) is insensitive as regards gas mixture. In contrast, γ_{ON} varies upon gas mixture. In the literature, a γ_{ON} higher than the γ_{OFF} is often observed and is usually ascribed to the ion bombardment that removes adsorbed atoms from the surface making active sites for adsorption. Indeed, ion bombardment is high during the phase ON and lacking during the post-discharge. Here, time resolved ion flux density measurements (Fig. 2b. and Table 1.) suggest that reaction probabilities on the walls are not only driven by the ion flux. We interpret this as an evidence of the importance of the walls surface chemistry.

Table 1: Characteristic times and reaction probabilities and ion flux for the studied gas mixture.

Gas mixture	τ_{ON} (ms)	τ_{OFF} (ms)	γ_{ON}	γ_{OFF} (ms)	Γ_{iON} (mA/cm ²)
H ₂	0.82	0.69	0.08	0.10	1.5
H ₂ / N ₂	1.64	0.59	0.03	0.19	0.9
CH ₄	0.55	0.91	0.73	0.10	1.1
CH ₄ / H ₂	0.52	0.80	0.31	0.10	0.9
CH ₄ / H ₂ / Ar / N ₂	1.49	0.69	0.04	0.12	

Conclusion

We carried out atomic H loss rate measurements by TR-OES and bring an evidence that the walls chemistry, and not only ion bombardment, has a strong influence on this rate. Measurements of N₂^{*} ($C^3\Pi_u \rightarrow B^3\Pi_g$), NH^{*} ($A^3\Pi \rightarrow X^3\Sigma^-$), CN^{*} ($B^2\Sigma \rightarrow X^2\Sigma$) and CH^{*} ($A^2\Delta \rightarrow X^2\Pi$) lines have also been done.

References

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