CHARACTERIZATION OF A MICROWAVE TIME-AFTERGLOW WORKING IN A CH₄-H₂-Ar GAS MIXTURE

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Abstract
A pulsed microwave H₂-CH₄-Ar discharge is investigated in order to study the variation of the species density with time, especially in the afterglow phase. A particular attention is paid to the behaviour of Ar, C₂ radical and hydrogen atom ground states. Results obtained from optical plasma diagnostic tools show a strong influence of thermal effects on the population density when the discharge power is off. The loss process of H-atoms in the afterglow is shown to be mainly due to the diffusion to and the recombination onto the chamber wall.

1. Introduction
The wide use of H₂-CH₄-Ar microwave plasma for CVD processes implies to have a good knowledge of the various kinetics occurring in the gas phase. In the particular interest in microwave plasma assisted chemical vapour deposition (MWPACVD) of diamond, previous works [1-4] have shown that pulsing the microwave input power greatly improves the quality and the growth rate of diamond thin films. In the case of a small size plasma reactor, it was shown that the deposition process can be optimised when using a power pulse duration of 1 ms with a repetition rate of 500 Hz [2-4]. Of course, this optimum is expected to depends on the chamber geometry and size as well as the working conditions. It is thus necessary to know the variation of the reactive species with the experiment parameters over a complete power pulse period. In this paper, we are particularly interested in the behaviour of heavy particles such as argon and C₂ radical, as well as in H-atom which is well known to be an efficient etching agent of graphite [5]. This presentation aims to give insights into the time variation of the investigated species and to explain some particular behaviour in terms of loss processes in the afterglow.

2. Experimental set-up
The experimental arrangement (figure 1) has been described in detail previously [3, 4]. Briefly speaking, the plasma chamber consists of a quartz tube (50 mm in diameter, 350 mm in length) that intersects a rectangular 2.45 GHz wave guide. The CH₄, H₂ and Ar gas concentration is ensured by means of mass flowmeters that are controlled so that to maintain the total pressure at a constant value (typically 8000 Pa) as well as the partial pressure of the different gases. The 0-1200 W microwave power supply is driven by a waveform generator, thus allowing the output peak power and the power pulse time-parameters (frequency and duty cycle) to be adjusted. The plasma diagnostic is performed by using time resolved optical

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emission spectroscopy (TROES), laser induced fluorescence (LIF) and the double pulse technique (DPT) [3, 4, 6, 7]. Whatever the diagnostic tool, the collected light is measured by means of a photomultiplier tube through a 500 mm focal length monochromator.

![Figure 1: Schematic drawing of the experimental arrangement. MW=Microwave power supply; PG=pressure gauge; VP=vacuum pump; SCT=short circuit stub; SH=substrate holder; OF=optical fibre.](image)

3. Results and discussion

3.1 Validation of the DPT

The characterization of the heavy species during the afterglow by the double pulse technique consists in re-exciting the ground state of the probed species to a radiative level by means of a short-duration power pulse (typically 100 μs) delayed with respect to the main discharge pulse. Nevertheless, it is important to ensure that the measured fluorescence signal is significant of the density of the species under consideration. For this, a comparison between LIF and DPT measurements of H-atom ground state variation during the afterglow has been carried out. The result of this comparison is reported on figure 2.

![Figure 2: Comparison between LIF and DPT measurements of H-atoms during the afterglow of a pure hydrogen plasma. Pressure=8000 Pa; Peak power=855 W; Plasma on-time=2 ms; Plasma off-time=18 ms](image)

Owing to the fact that LIF does not disturb the discharge, the good agreement of the two curves clearly shows that

i) the probing pulse does not perturb the main discharge pulse

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ii) the DPT measurements are significant of the density variation of the probed species whatever the delay between the main discharge pulse and the probing pulse.

3.2 Variation of C₂ and Ar species during the afterglow.

The study of C₂ shows that the C₂ density strongly decreases in the early afterglow (t < 1 ms) after the main power pulse is switched off (fig. 3). This sharp decrease is then followed by an increase in C₂ density in the late afterglow (t > 1 ms). This phenomenon is also observed when working with no substrate holder inside the plasma chamber (fig. 3b). Nevertheless, the increase in density is less marked than with the substrate holder in place (fig. 3a). By looking at the reaction rates of the kinetic processes involving C₂ [8] (especially the collision between neutral species), it appears that when the input power is off, the characteristic times of the C₂ loss processes are much greater than those of C₂ production. In other words, these reaction rates easily explain the sharp decrease of C₂ in the early afterglow. On the other hand, the increase in C₂ for time greater than 1 ms can not be attributed to creation terms. It is thus necessary to find another explanation for this phenomenon.

![Graph showing time variation of the fluorescence signal of C₂ during the afterglow with (a) and without (b) substrate holder. P=8000 Pa; Peak Power=855 W; Plasma on-time=2 ms; Off-time=18 ms; Gas mixture=H₂(87)-CH₄(10)-Ar(3).

Figure 3: Time variation of the fluorescence signal of C₂ during the afterglow with (a) and without (b) substrate holder. P=8000 Pa; Peak Power=855 W; Plasma on-time=2 ms; Off-time=18 ms; Gas mixture=H₂(87)-CH₄(10)-Ar(3)]

Such an increase in species density has been also noted on argon species as can be seen on figure 4a. In this case, the increase in argon density is observed over 10 ms in the afterglow. The excitation of the upper level of the observed transition by means of DPT is achieved through electron collisions with argon ground state. Thus, the fluorescence intensity can be written:

\[
I = K(\lambda) \Delta V \frac{A \Delta \Omega}{4\pi} A \left[ [Ar_o] n_e \right] \int_{-\infty}^{\infty} \sigma(v) v f(v) dv
\]

where K(\lambda), \Delta V, \Delta \Omega and A are constants that represent the spectral response of the optical device, the volume of plasma investigated, the solid angle of observation and the transition probability respectively; [Ar_o] stands for the density of argon ground state, n_e is the electron density, \sigma(v) is the excitation cross section and f(v) is the electron velocity distribution.
function. The comparison between LIF and DPT measurements has shown that the excitation term \(n_e \int_{\nu_1}^{\nu_2} \sigma(v) f(v) \, dv\) provided by the probing pulse is constant over the whole afterglow [4]. Indeed, with DPT, the excitation process of H\((n=1)\) and Ar\(_6\) are similar and due to electron collisions (note also that the excitation energies are also comparable). As a consequence, the increase in argon DPT measurement can only be ascribed to an increase in [Ar\(_6\)] that results from the cooling of the neutral gas during the afterglow. Such a thermal effect also take place in the reverse way during the discharge phase (fig. 4b). In fact, when the power is switched on, the neutral gas temperature is rather low and the argon density is relatively high. Consequently, the observed emission line of argon exhibits a marked peak followed by a decrease resulting from the gas heating, up to a stationary value that is reached when the thermal equilibrium is achieved. This cooling of the neutral gas is also responsible for the increase in C\(_2\) as reported in figure 3. Furthermore, the substrate holder that is plasma heated up to 1120 K acts as a cold part with respect to the plasma, the temperature of which is close to 2000 K in the discharge regime [9]. This explains that the effect of the cooling of the neutral gas is more pronounced when the substrate holder is inserted in the plasma chamber.

![Figure 4: Time variation of argon density: (a) afterglow; (b) discharge regime. Same conditions as in figure 3 except gas mixture H\(_2\)(97)-Ar(3).](image)

### 3.3 H-atom variation during the afterglow

After the main discharge pulse interruption, the decay of the H-atom density exhibits two different loss rates and one can question about the processes that are responsible for this phenomenon (fig. 5). In the afterglow, the main loss processes of H-atoms are

1. **Volume recombination (H+H+H\(_2\) \rightarrow 2\(\text{H}_2\))** leading to
   \[
   \frac{d[H]}{dt} = -k_v[H]^2[H_2]
   \]
   where the recombination rate can be expressed as a function of the gas temperature [10]
   \[
   k_v = 2.7 \times 10^{31} T_{\text{g}}^{-0.6}
   \]

With the typical working conditions, the dissociation rate of molecular hydrogen (\(\alpha\)) is less than 2% [11, 12] and we can assume a constant concentration of H\(_2\), the value of which is given by the ideal gas law.

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\[ [H_2] = \frac{[H_2]_0}{P/k_B T_g} \quad (4) \]

Integration of eq. (2) gives the variation of H-atom density with time:
\[ [H]_0/[H] = 1 + k_r[H_2]_0[H]_0 t \quad (5) \]

The volume recombination mainly occurs at high density, that is in the early afterglow. The measurement of the slope of the fast decay process leads to
\[ k_r[H_2]_0[H]_0 = 7000 \text{ s}^{-1} \quad (6) \]

On the other hand, the H-atom density at \( t=0 \) can be expresses as
\[ [H]_0 = 2\alpha[H_2]_0 \quad (7) \]

The combination of equations (3), (4), (6) and (7) allows the determination of \( \alpha \):
\[ \alpha = 3.87 \times 10^{-8} T_g^{2.6} \quad (8) \]

\[ \text{Figure 5 : Variation of H-atom relative density in the afterglow. Same conditions as in figure 3} \]

Thus, assuming that the volume recombination is the dominant loss process in the early afterglow would lead to a dissociation rate greater than 100% for a gas temperature greater than 700 K. As mentioned above, with the conditions used, the gas temperature is around 2000 K and \( \alpha \) is less than 2%. Consequently, the volume recombination is not the dominant loss process of H-atoms and it can be neglected.

(ii) Thermal agitation and recombination onto the wall \( (H_{\text{gas}} + H_{\text{wall}} \rightarrow H_2) \) leading to [13]
\[ \frac{d[H]}{dt} = -\gamma <v_{H}>[H]/2R \quad (9) \]

where \( R \) represents the tube radius, \( \gamma \) is the sticking coefficient of H-atom on the chamber wall and \( <v_{H}> \) is the mean H-atom velocity. Nevertheless, eq. (9) is only valid for a collisionless plasma, that is when the atom mean free path is of the same order of magnitude than the chamber dimensions. In the present case, with \( R=25 \text{ mm} \) and \( P=8000 \text{ Pa} \), the mean free path of H-atoms ranges from 2\( \mu \text{m} \) (at \( T_g=300\text{K} \)) to 15\( \mu \text{m} \) (at \( T_g=2000\text{K} \)). It follows that the collisions can not be neglected and thus thermal agitation is not the main transport process of H-atoms towards the walls.

(iii) Diffusion to and recombination onto the walls \( (H_{\text{gas}} + H_{\text{wall}} \rightarrow H_2) \) which is described by
\[ \frac{\partial [H]}{\partial t} = D \Delta [H] \]  
(10)

where the diffusion coefficient can be expressed as [14]

\[ D = 4.8876 \times 10^{-3} T_n^{1.2} T_p^{0.8} \]  
(11)

During the afterglow, the gas temperature as well as the H-atom one vary with time and so does the diffusion coefficient. As a consequence, the two slopes observed on the decay of the H-atom density are not due to two different loss processes but to the only diffusion term that decreases with increasing time in the afterglow.

4. Conclusion

Time-resolved measurements of the relative H-atom density has pointed out that the main loss process of H-atoms is the diffusion towards the chamber walls on which atoms recombine. This transport process depends on the density gradient, the gas temperature and the kinetic temperature of H-atoms as well. Because of the cooling of the neutral gas when the power is switched off, it results that the diffusion term decreases with time in the afterglow.

Moreover, the study of an argon line has led to show that the variation of the gas temperature with time is phenomenon of prime importance in such pulsed discharges. In fact, it implies a strong variation of the local densities. This result allowed us to explain the increase in \( C_2 \) relative concentration observed in the late afterglow.

References