Electrical and optical characterization of a capacitively-coupled RF plasma with a pulsed argon gas injection

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Abstract: Nanocomposite thin film deposition using a reactor-injector of nanoparticles implies a pulsed gas injection. In a plasma, this can affect the behavior of the downstream process. Here, the case of an asymmetric low-pressure RF plasma with a pulsed argon gas injection is analyzed by electrical and optical emission spectroscopy measurements. It is found that this injection mode can highly affect the plasma stability: both the electron temperature and density are modified during the rise and the decrease of the gas pressure. A new injection mode combining continuous and pulsed injections is proposed to obtain more stable conditions.

Keywords: RF plasma, Reactor-injector, Pulsed gas injection, emission spectroscopy

1. Introduction

In recent years, various applications require the use of nanocomposites (NCs): indeed, the presence of at least 2 phases leads to multifunctional properties that can be valuable in a wide variety of industries.

Plasma-based processes allow to form NC thin films. There are many pathways to plasma-deposit these materials, the simplest dealing with the direct introduction of nanoparticles (NPs) in the plasma phase with the matrix precursor. For example, preformed NPs mixed in a solution with the matrix precursor can be used. These suspensions of NPs can be directly evaporated in the plasma reactor or sprayed as an aerosol [1]. While the first method is generally difficult in the presence of NPs, aerosol allows to inject non-volatile molecules as well as suspensions at room or even lower temperatures [2]. Nevertheless, sprays generally lead to agglomerates of NPs [3]. Indeed, NPs in the droplets can grow during the process (solution, injection and plasma process), inducing the deposition of NCs with a distribution of reinforcements larger than the one of the initial NPs as shown in the figure 1.a.

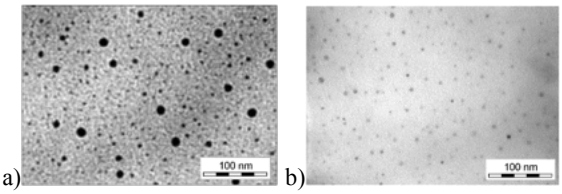


Fig. 1. SEM images of plasma-deposited NC thin films deposited using (a) a suspension of NPs and (b) a reactor-injector of NPs.

Recently, a new method called "reactor-injector" has been developed [4]. It allows to synthetize the NPs immediately before their injection into the plasma reactor. This results in a safer-by-design process for plasma-assisted deposition of NC thin films and further allows the deposition of isolated (*i.e.* non-aggregated) and really small (6 nm) NPs embedded in a matrix (figure 1.b) [4].

By design, the reactor-injector works in a pulsed gas injection regime that can bring significant variations of the gas pressure during plasma deposition. Such variations can affect the plasma kinetics and can even introduce plasma instabilities. Here, we report a fundamental study on the impact of a pulsed injection of a non-reactive gas on the behaviour of a low-pressure RF plasma using electrical and optical diagnostics. Besides the investigation of underlying plasma physics, one of the main objective is to establish conditions where the reactor-injector only slightly affect the plasma characteristics.

2. Experimental set up

Experiments were performed in an asymmetric RF (13.56 MHz) plasma reactor. This system consists in a 300 mm RF biased bottom electrode and a shower-like top electrode for spatially homogeneous gas injection. In this study, nominally pure argon is used. It can be introduced through the shower electrode either continuously using a mass flowmeter or through pulses using the reactor-injector.

As shown in Figure 2, a number of parameters can be controlled on the reactor-injector, namely, the injector opening times t_{in} and t_{out} as well as the frequency of the opening times f. Over the range of experimental conditions investigated (t_{in}=2 ms, t_{out}=10 ms and f values between 0.1 and 10 Hz), this results in pulsed argon gas injection into the low-pressure argon plasma with pulse durations from 1 to 0.5 s. The pressure, p, the incident power, P_{inc}, the reflected power, P_{ref}, and the self-bias voltage, V_{bias}, are

recorded along the process for several periods of the gas injection. Simultaneously, optical emission spectra in the 350-850 nm wavelength range are continuously recorded using a low-resolution optical emission spectrometer with an integration time of 1 s for the pulsed condition and 0.2 s for the continuous plus pulsed one.

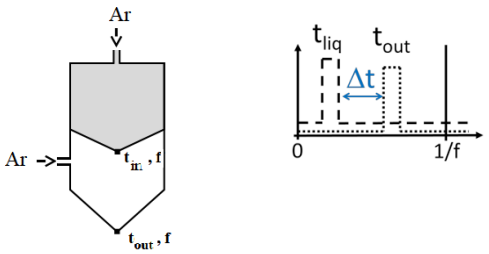


Fig. 2. Principle of the reactor-injector and its parameters namely, the injector opening times t_{in} and t_{out} as well as the frequency f.

3. Effect of pulsed injection parameters

Figure 3 reports pressure data in the plasma reactor over one period of the gas injection pulses for t_{in} = 2 ms, t_{out} = 10 ms and f = 0.1 Hz (red curve): from the steady-state pressure p_0, the pressure sharply increases with a variation Δp after the pulsed gas injection and then progressively returns with a much slower rate to the steady-state pressure.

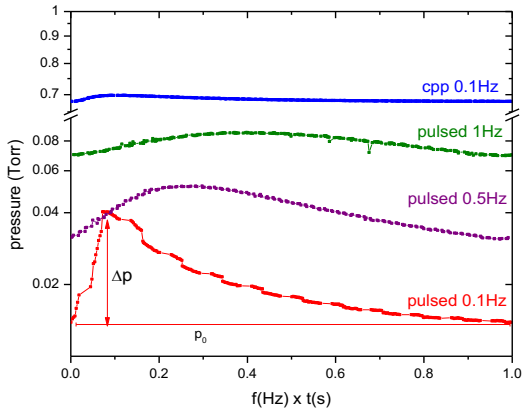


Fig. 3. Evolution of the pressure induced by gas injection pulses for different frequency. The time scale is multiplied by the frequency to highlight variations for different frequencies.

While t_{in} and t_{out} in the few ms range does not really affect p_0 and Δp, Figure 3 indicates that the frequency f leads to different pressure regimes. The higher the frequency is, the higher is the steady-state pressure and the lower is the pressure variation during each pulse. These aspects are summarized in Figure 4a for frequencies between 0.1 and 5 Hz. For example, between 0.1 and 5 Hz, p_0 increases from 0.014 to 0.42 Torr while Δp decreases from 0.026 to 0.001 Torr. Variations of the absorbed power, self-bias voltage, and excitation temperature can also be seen in Figures 4b, 4c, and 4d. These aspects will be discussed in the next sections.

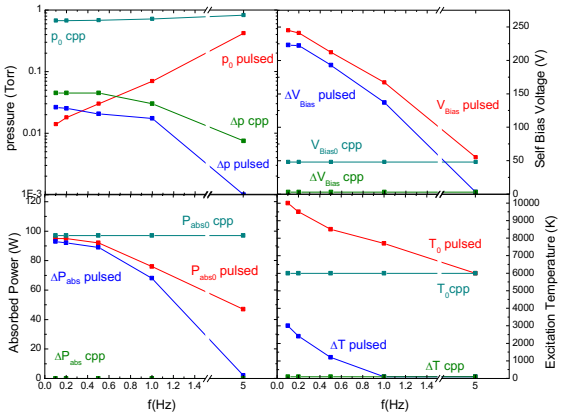


Fig. 4. Evolution of the pressure, the absorbed power, the bias voltage, the excitation temperature and their variation during the pulse for various frequencies in pulsed conditions. For comparison, the mode continuous + pulse discussed later in Section 6 is also added.

4. Electrical characterization

The pressure variations discussed in the previous section affect the discharge electrical parameters. For example, Figure 5 reports the variation of the absorbed power (red curve), defined as $P_{abs} = P_{inc} - P_{ref}$ (where P_{inc} and P_{ref} are the incident and reflected powers, respectively) and the self-bias voltage (green curve) as a function of time over one period for t_{in} = 2 ms, t_{out} = 10 ms, and f = 0.1 Hz. A comparison between Figures 3 and 5 reveals that the variation of the pressure around 1 s after the pulsed gas injection causes instabilities in the absorbed power and the self-bias voltage during about 3 s. In addition, the absorbed power is maximized only less than 50 % of the injection period. Therefore, it becomes complicated to achieve stable plasma conditions at low frequency.

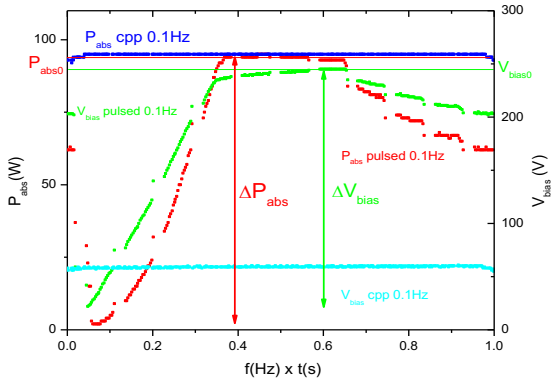


Fig.5. Evolution of the absorbed power (red) and of the self-bias voltage (green) induced by gas injection pulses at f=0.1Hz. As in Fig. 3, the time scale is multiplied by the frequency. For comparison, the mode continuous + pulse discussed later in Section 6 is also added (blue for the absorbed power and cyan for the self-bias voltage).

In line with the pressure variations displayed in Figure 3, steady-state values of the absorbed power, P_{abs0}, and self-bias voltage, V_{bias0}, as well as their variations during each gas injection pulses, ΔP_{abs} and ΔV_{bias}, can also be defined in Figure 5. Figure 4 reports their evolution with the frequency. In good agreement with the classical behavior of RF plasmas, the absorbed power and the self-bias voltage reveal comparable trends. More specifically, both P_{abs0} and V_{bias0} decrease with increasing frequency, *i.e.* when increasing the steady-state pressure p_0. In addition, at higher frequency, *i.e.* when the pulsed gas injection slightly modifies the working pressure corresponding to an injection mode quasi-continuous, the variations of the absorbed power and of the self-bias voltage tend to decrease. This means that injection at higher frequency produce more stable plasmas. This aspect was also confirmed by optical emission spectroscopy analysis as described in the next section.

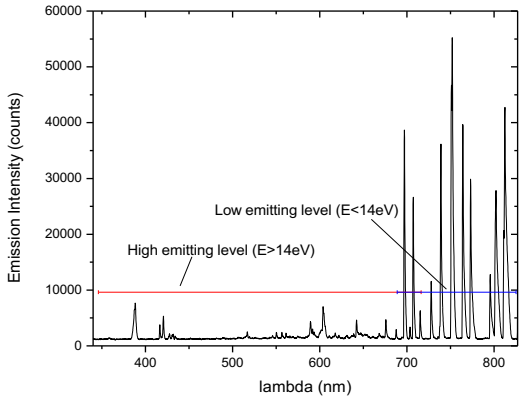
5. Optical characterization

Optical emission spectroscopy recorded along the line-of-sight in the interelectrode gap has been carried out to gain insights into the plasma characteristics over the pulsed gas injection period. A typical spectrum is reported in Figure 6a: among the different argon lines emanating from the argon 2p-to-1s transitions (Paschen notation), the 750, 763 and 811 nm lines are the more intense.

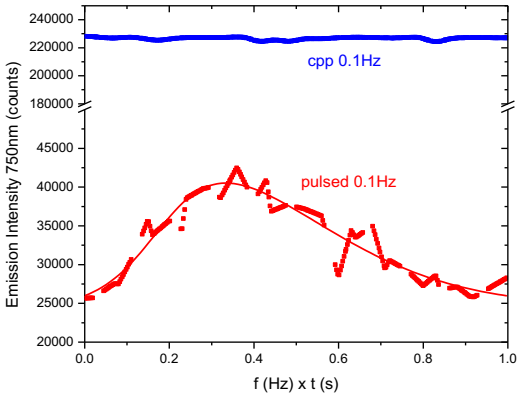
Figure 6b reports the time evolution of the 750 nm line intensity recorded over one period of the gas injection pulses for t_{in} = 2 ms, t_{out} = 10 ms and f = 0.1 Hz. Similarly to the values of the pressure, the absorbed power and the self-bias voltage displayed in Figures 3 and 5, the line intensity shows significant variations in the pulsed mode (red curve). In particular, the line intensity reaches a maximum beyond the maximum of the gas pressure when the absorbed power is maximized; this suggests that the pulse gas injection significantly impacts the plasma density.

This aspect was examined in more details by plotting the ratio of the line intensity over the gas pressure (assumed proportional to the argon neutral atom density). Assuming that the argon $2p_1$ level leading to the emission at 750 nm is mainly populated by electron-impact excitation on ground state argon atoms and is mainly lost by spontaneous emission in an optically thin media, this ratio becomes solely linked to the product of the electron number density and the reaction rate for electron-impact excitation (which depends on the electron temperature assuming Maxwellian electron energy distribution function). The results are presented Figure 7.a. Clearly, the ratio sharply decreases early in the gas injection pulse and then reaches a maximum when the absorbed power is maximized. This behavior suggests that both the electron temperature and density vary over the period of the gas injection pulses.

To gain insights into the time evolution of the electron temperature, the excitation temperature was calculated using the argon high-energy levels (red lines in Figure 6.a) and a simple Boltzmann diagram [5]. Figure 7.b reports the time evolution of the excitation temperature obtained over one period of the gas injection pulses for t_{in}=2 ms, t_{out}=10 ms and f=0.1 Hz. As can be seen, the excitation temperature drops from 10,000 to 7000 K early in the pulse cycle; a feature directly linked to the rise of the gas pressure. Indeed, in low-pressure argon plasmas in which charged species are mostly created by electron-impact ionization on ground state argon atoms and are lost by diffusion and recombination on the plasma reactor walls (here, the top and bottom electrodes), the electron temperature is expected to decrease with increasing pressure [6], in very good agreement with the trend of the excitation temperature displayed in Figure 7.b.



a)



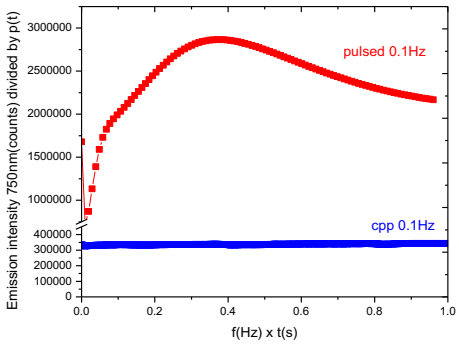
b)

Fig.6. a) Typical spectrum of an argon plasma produced in continuous plus pulsed mode at 0.1 Hz. The high and low emitting levels are described by the red and the blue lines. To highlight the variations along the pulse, the evolutions of the argon 750nm line in pulsed and continuous plus pulsed modes are reported in b).

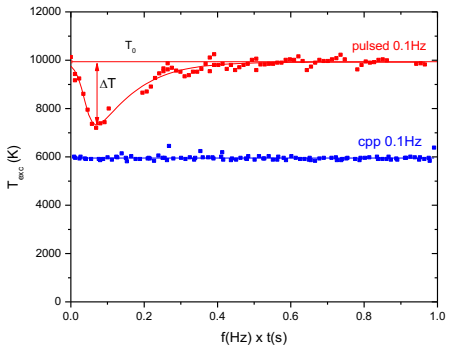
By comparing the results presented in Figure 7.a with those displayed in Figure 7.b, it seems that only the first part of the I_{750}/p curve, from 0 to 4 seconds, is influenced by the corresponding variation of the excitation temperature or the electron temperature. It therefore suggests that the remaining variations of I_{750}/p are mostly linked to temporal variations of the electron density.

Similarly, with the previous data, a steady-state excitation temperature, T_0, and its variation after the pulsed

gas injection, ΔT, can be defined in Figure 7.b. The results are reported in Figure 4. Again, both values decrease with increasing frequency. This result can readily be linked to the corresponding variations of the gas pressure and the expected behavior of the electron temperature in diffusion-controlled plasmas: as the pressure increases, the electron temperature decreases [6].



a)



b)

Fig.7. Evolution over an injection period of a) the 750nm line intensity divided by the pressure and of b) the excitation temperature as determined from Boltzmann diagram.

6. Alternative injection mode

From the results presented in the previous sections, variations of the plasma properties seem lower when the reactor-injector leads to relatively high pressures. However, with a high repetition rate, the production of NPs in the reactor-injector can become non-optimal. Hence, it is important to find another way to stabilize the plasma properties with the pulsed gas injection. In this context, a continuous argon flow rate was used along with a pulsed gas injection at 0.1 Hz (with t_{in} = 2 ms, t_{out} = 10 ms). Pressure data in the plasma reactor over one period of the gas injection for this new operation mode of the reactor-injector (continuous + pulse, or simply cpp) are shown in Figure 3. In contrast to the pulsed gas injection mode, no significant pressure variations were observed in the cpp mode. Consequently, no significant variations of the absorbed power (Figure 5), self-bias voltage (Figure 5), argon emission intensity (Figure 6b), electron density and temperature (Figure 7a), and excitation temperature (Figure 7b) could be observed. For the I_{750}/p ratio and the excitation temperature plotted in Figure 7, the values are lower in the CPP mode than in the pulsed mode; a feature linked to the lower electron temperatures due to the higher pressures [6]. As shown in Figure 4, the pressure, absorbed power, self-bias voltage, and excitation temperature further remained fairly constant over a wide range of frequency (0.1 to 5 Hz).

7. Conclusions and perspectives

Pulsed injection of gases at low frequency in a low-pressure capacitively-coupled plasma reactor significantly destabilizes the plasma. Specifically, the self-bias voltage controlling the average energy of the ions impinging onto the substrate surface as well as the electron density and temperature driving the plasma physics and chemistry vary meaningfully over the pulse period. This suggests that the plasma treatment is not really optimized such that the plasma deposition dynamics of NC thin films could also be non-optimized. To circumvent this limitation, a new mode of operation of the reactor-injector mixing a continuous injection with the pulsed injection was proposed. Through this new mode, temporal variations of the pressure and of the plasma properties can be strongly minimized, a very promising result for plasma deposition applications. In particular, similar behaviors were observed when adding, in the pulsed injection, polymerizing gases such as pentane for plasma-enhanced chemical vapor deposition of organic coatings. Similar studies in the presence of NPs in the gas phase are in progress.

8. References

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