Low pressure cold plasma assisted dust nanoparticles metrology

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Interests in dust particles characterization, nowadays is becoming a hot topic. Indeed synthesis and use of nanoparticles of different chemical compositions is now concerning many domains and still in development. This requires accurate method tools for the detection, global characterization in terms of size, concentration, morphology and optical properties in order to evaluate their toxicity and prevent any accidents. A simple and accurate method for the measurement of these two parameters in pure argon and argon-acetylene plasmas generated in a capacitively coupled radiofrequency discharge is presented. A strong correlation between the discharge impedance and the dust particle size and concentration is emphasized and a theoretical model is proposed to explain the phenomenon. This electrical method is compared to two other methods based on laser light scattering is achieved.

1. Introduction

Plasma nanotechnology is nowadays a domain that has very rapid development. Very active research programs are under way that bring to the fore excellent results and advances. Researchers focused their interests on the interaction of the plasma and more precisely the reactive species that are produced in the gas phase in the plasma with surfaces in order to produce nanostructures with different properties and for different applications. Top-down technology has been widely explored and used in order to reduce the device sizes. At the present time this technology is facing very difficult problems when reaching critical dimension of few nanometres.

Dust particles nucleating and growing up in plasmas were considered as very harmful. In fact when occurring in low pressure plasmas used for etching or thin layers deposition they can induce irremediable defects in the devices under fabrication. The situation is becoming serious due to the miniaturization of the devices. As defined by the International Technology Roadmap for Semiconductors (ITRS), the sizes of the "killer" particles is now about 20 nm and will even less in the near future. Huge efforts have been devoted to understand the dust particle nucleation and growth phenomena. The knowledge acquired allows the use of dusty plasma as a tool for the development of different applications based on the synthesis of nanoparticles tailored in different kind of plasmas such as energy production (photovoltaic [1, 2, 3] in the second and third generation), hydrogen conversion (nanocatalysts) [4] and thermoelectricity [5]. In fact, plasma synthesised nanoparticles, with 100 nm in diameter, can exhibit a large specific area more than 100 m^2/g [4].

In this contribution we will concentrate our attention on dust particles occurring in low-pressure plasmas generated by a radio-frequency discharge. We shall give a brief overview on the nucleation and growth mechanisms. These nanoparticles induce when they appear in the plasma drastic changes in the plasma and discharge characteristics [6-8] due to the strong electron attachment. The main modifications concern the plasma resistance and the plasma sheath capacitance. These modifications can be used to detect the occurrence of the nanoparticles in the plasma bulk when their sizes are of the order of less than 5 nm.

Rising also is the need of detection and metrology techniques of such nanoparticles either for the monitoring of their synthesis for dedicated uses or for environmental and person's health protection purposes. In fact right now there is a lack of regulation codes and rules for nanoparticles handling and working conditions. Therefore it is very urgent to develop new methods and tools for the nanoparticles detection and metrology in dry environment and in terms of size, concentration, chemical composition, morphology etc.

In this contribution we will present three methods allowing to measure the mean size and concentration, size distribution and optical properties based on the analysis of the modifications the dust nanoparticles are inducing on the electrical discharge and plasma characteristics when they grow up or are injected in the gas phase of a plasma generated in a capacitively coupled radiofrequency

(CCRF). The results will be compared to those obtained thanks to the use of multi-angle laser light scattering (MALLS). Finally the size distribution is determined by plasma-assisted sedimentation (PAS). The comparison of these results allows also the determination of the optical characteristics of the dust particles.

2. Results and discussions

The first method in question in this contribution, which does not require any current/voltage phase shift measurement, could be appropriate to monitor in real time the plasma coupled power in any CCRF discharge with a very good accuracy. Moreover, the underlined relationship between the plasma/electrode sheath impedance and the dust particle size could be used to follow in real time the evolution of the size of the dust particles using plasma [9]. A very good correlation between the evolution of the dust particles size in the plasma and the increase of the plasma/electrode sheath capacitance (fig. 1) suggests that charged dust particles induce an electrostatic force on the plasma sheath. An analytical model is proposed in order to take this phenomenon into account in future dusty plasma electrical modeling [10].

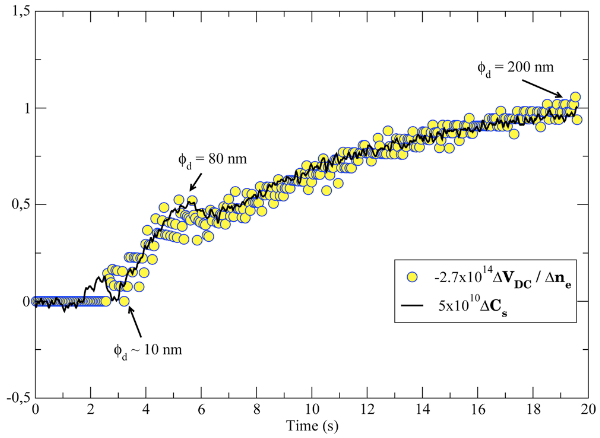

Fig. 1: *Correlation between sheath capacitance and dust particles mean size formed in low-pressure plasma.*

It is also possible to determine the effective power coupled to the plasma by recording the current/voltage waveforms without any need to their phase shift. The obtained results are compared to the ones given by the subtractive method (Fig.2).

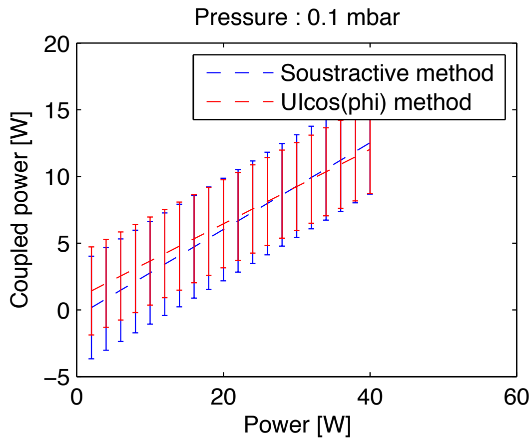

Fig. 2: *effective power injected in the plasma*

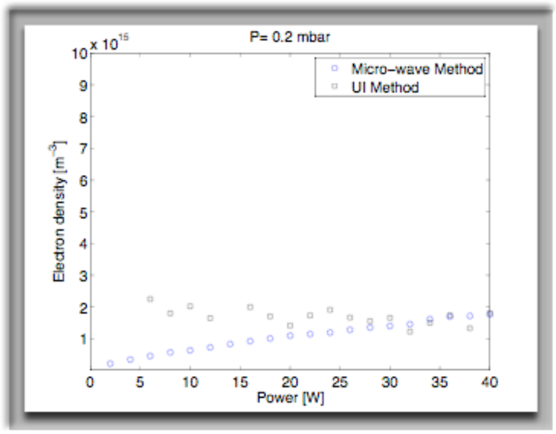

Fig. 3: *Comparison of the electron densities obtained in the same plasma using effective coupled power and microwave resonant cavity method.*

On the basis of the global model of M Lieberman and knowing the time evolution of this power it is possible to deduce the one of the evolution of the mean value of the electron density over the plasma volume of the plasma and even its changes induced by the presence of dust particles (fig.3). As shown by G. Wattieaux et al [10] this can be used to deduce the mean size and concentration of these particles

Thus the variations induced by the presence of dust particles can be evaluated and used to determine their average size and concentration. In fact the changes induced are related to the electron attachment on the dust particles. Assuming spherical particles it is possible to express the total electron loss by attachment as

$$\Delta n_e = \frac{2\pi\epsilon_0}{q}(V_P - V_d)\phi_d \cdot n_d.$$

where q, V_p, V_d, $Ø_d$ and n_d are respectively the elementary charge, plasma potential, floating potential of the dust particles, their diameter and number density. This electron density variation will have a drastic effect on the self-bias voltage and its variation can be written as

$$\Delta V_{DC} = K\Phi_d^2.n_n$$

These variations can be related to the mean particle size and concentration as:

$$\frac{\Delta V_{DC}}{\Delta n_e} = K_\Phi.\Phi_d \qquad \text{and} \qquad \frac{(\Delta n_e)^2}{\Delta V_{DC}} = K_n.n_d$$

with $K_Ø$ and K_n are calibration constants. It is thus clear that if we can measure the electron density variations related to the presence of dust particles in the plasma bulk it will allow to determine their size and concentration.

This method was used to measure the size and concentration of carbon particles grown in argon-methane gas mixture low-pressure cold plasma. Figure 4 gives the time evolution of these two parameters.

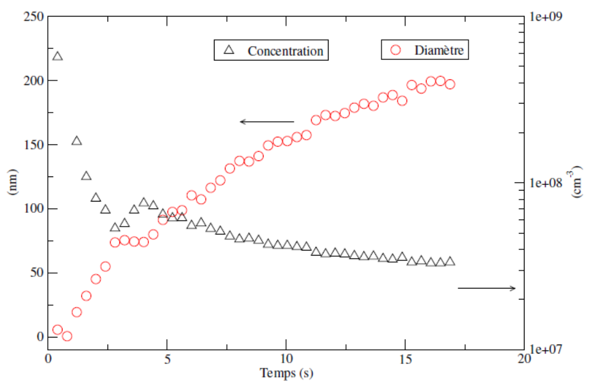

Fig. 4: *Time evolution of carbon dust particle mean size and concentration grown in argon-methane low-pressure plasma.*

Therefore the electron density measurement method based on the measurements of the effective coupled power can be used to size the dust particles trapped in the plasma bulk.

The reactor used to perform these studies has 16 faces and thus allows recording of the scattered light for fifteen different angles located at 22.5° apart from each other. Figure 5 gives an example of measured size given by MALLS and electrical method for carbon particles growing in argon-acetylene plasma. For long plasma duration we observe a difference between the two methods. This is due to the fact the electrical one gives an average size over the total volume of the plasma while the MALLS gives the size in the few mm^3 scattering volume located in the centre of the reactor.

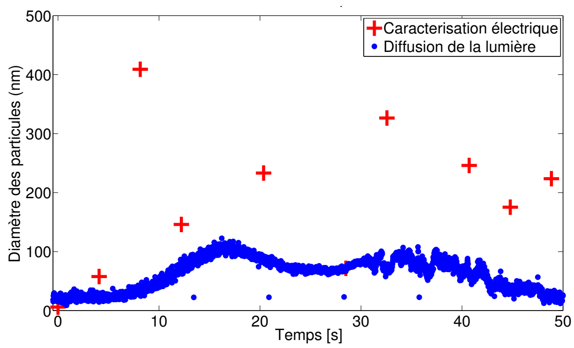

Fig. 5: *Comparison of the measured sizes of carbon nanoparticles by electrical method (red crosses) and MALLS (blue dots).*

It is well known that dust nanoparticles remain trapped as long as the plasma is on. They levitate close to the lower charge space sheath. As soon as the plasma is turned off they fall down and thus sediment on the lower electrode. We drilled a 1 cm small hole in diameter in the centre of the electrode bellow which we located a sedimentation cell equipped with two laser diodes and two photodiodes at 90° apart Fig. 6). By this way we can measure the sedimentation velocity at low pressure of the nanoparticles. At these pressure conditions this velocity is directly proportional to the nanoparticle size [11, 12]. Therefore when the particles are released by turning off the plasma they fall down and cross the two laser beams. From the signals collected by the two photodiodes it is possible to determine the velocity distribution and thus the size distribution of the nanoparticles composing the dust particles falling cloud.

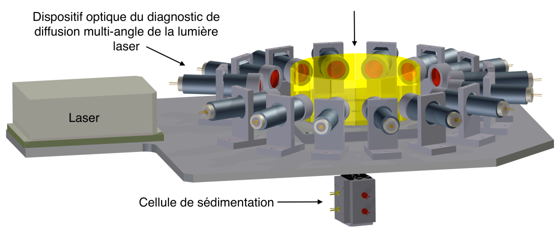

Fig. 6: *Plasma-assisted nanoparticles sedimentation set-up.*

Figure 7 gives the size distribution of the particles formed in the ar-SiH4 gas mixture and 10 seconds plasma duration. It shows the comparison of the size distributions obtained thanks to transmission electron microscopy (TEM) and plasma-assisted sedimentation. It is clear from this figure that we have a good agreement between the two methods [13] and that PAS has a size resolution of about 1 nm. The calculated mean size from these distributions is also in good agreement with those obtained by MALLS and electrical method.

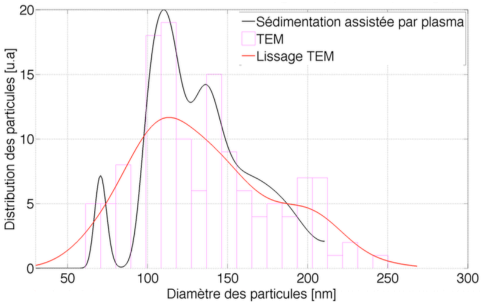

Fig. 7: *Comparison of the nanoparticles size distributions obtained by TEM and by PAS.e.*

Conclusion

In this contribution we compared three different methods to measure the average size and concentration of dust nanoparticles levitating in a low-pressure cold plasma. The first one is based on the analysis of the changes induced by the nanoparticles on the electrical parameters of the discharge and plasma. The second one is the multi-angles laser light scattering and the third one corresponds to the analysis of the sedimentation of the nanoparticles when the plasma is turned off. The obtained results are in good agreement for particles with sizes under 100 nm.

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