Study of hydrocarbon dust particle formation in Ar-CH$_4$ radiofrequency low pressure discharge

A. Mezeghrane[1,2], L. Couëdel[1], G. Wattieaux[1], M. Mikikian[1], O. Lamrous[2], Y. Tessier[1], L. Boufendi[1]

[1]*GREMI (Groupe de Recherches sur l'Energétique des Milieux Ionisés), Orléans, France*

[2]*LPCQ (Laboratoire de Physique et Chimie Quantique), Université M. Mammeri de Tizi-Ouzou,*

Algérie

ABSTRACT

The aim of this paper is to contribute to improve the knowledge concerning the growth steps of hydrocarbon dust particles in Ar-CH$_4$ plasma. To achieve this aim, we monitored the plasma impedance modification, due to the particle formation, by measuring the time-evolution of the self bias voltage, the current third harmonic and the electron density. Emission Spectroscopy turns out to be a good tool for estimating the electron temperature. While, Transmission and Scanning Electron Microscopy are used to characterize the morphology and the size of collected powders.

The correlation between the electrical parameters shows clearly when the accumulation and coagulation phases occur. It is also obvious that the growth kinetics of this kind of dust particles is like in silane (a four step process) but the time scale is quite different. The electron temperature variations emphasise the electric field exaltation in the plasma bulk, resulting from the $\alpha \rightarrow \gamma'$ transition.

I.   INTRODUCTION

Dust formation can be observed in various processing discharges such as sputtering, etching, and plasma enhanced chemical vapour deposition (PECVD) in reactive gases such as silane, methane and acetylene. The dust growth kinetics and plasma chemistry in silane plasmas, have been extensively studied [1, 2]. In contrast and despite the importance of discharges in hydrocarbons, very little research is devoted to study the nucleation and growth of dust particles in these discharges. It is important to note that powders are spontaneously produced in acetylene (C$_2$H$_2$) plasmas while it is difficult to initiate them in methane (CH$_4$) plasmas [3, 4]. In this paper, our efforts are focused on the identification of dust particle growth steps and the effect of injected power on their formation kinetics.

II.   EXPERIMENTAL CONDITIONS AND DIAGNOSTICS

The present work was carried out in Ar-CH$_4$ gas mixture capacitively coupled radio frequency discharge. The experimental set-up was described in detail elsewhere [5]. Typical experimental conditions, the total pressure and methane ratio in argon , are kept constant at respectively 1.1 mbar and 2%, the RF power varies from 10 to 30W and the gas is at room temperature. The discharge is modulated by alternating T$_{on}$ and T$_{off}$ periods. A right choice of methane proportion and RF-power is

crucial to produce, at relatively short time (less than 20 s), powders with mean sizes larger than 100 nm in radius. These dust particles are white and are produced without any added amount of acetylene or applied transient high power [4].

S. Stoykov et al. and S. Hong et al. [3, 4] reported that the formation of primary clusters in methane plasma depends on the presence of a critical amount of acetylene (C_2H_2). On the other hand, chemical reactions leading to the formation of acetylene, in methane plasma, are always occurring but with low reaction rate (this conversion rate depends on the input power and also on the pressure [6]). In our experimental conditions, the conversion rate seems to be relatively sufficient to reach the acetylene critical density.

Electron density is measured using the discharge box as a microwave resonant cavity by following the TM 110 cavity mode during the dust particle formation. The frequency scan step was fixed at $0.5 MHz$ in order to have a sufficient time resolution for the electron density measurement during the T_{ON} RF-cycle. Then, the maximum transmitted microwave signal amplitude is measured at different times. Each maximum is associated with the resonance frequency at corresponding time. Finally, the electron density is determined using the following relation:

$$n_e(t) = \frac{2m_e \varepsilon_0 (2\pi f(t))^2}{e^2} \frac{\Delta f(t)}{f_0} \tag{1}$$

where $f(t)$ is the resonance frequency at time t, $\Delta f(t) = f(t) - f_0$ the frequency shift and f_0 the resonance frequency without plasma $\left(f_0 = 2710 MHz \right)$.

III. RESULTS AND DISCUSSION

The obtained results, for different RF-powers, are shown on figures 1 and 2. Figure 1 shows time evolution of the electron density (n_e), the self bias voltage (V_{dc}) and the third harmonic amplitude (3H) in Ar-CH$_4$ plasma, with an applied RF peak-to-peak voltage of 300 V and a gas mixture ratio of (98 : 2). For $t \prec t_1$, the electron density varies slightly like V_{dc} and 3H. This time range is attributed to the formation and accumulation phase of nanoparticles.

When comparing the different profiles of n_e (figures 1 and 2), one can note that this time interval increases with power. However n_e profile, corresponding to $V_{p-p}(RF) = 250V$, exhibits a different behaviour. This is may be due to the fact that the reactor walls were not well cleaned in this case. Indeed, wall cleaness can have an influence on particles growth kinetics. For this reason, a particular attention is paid to the wall cleaning after few runs. The drastic n_e drop, observed at t_1, corresponds to a fast coagulation phase. After this coagulation, n_e varies slowly up to t_2. During this phase, the powders grow up mainly by radical accretion. Another n_e decrease (duration ~ 1s) is observed at t_2, probably due to a second coagulation. Around t_2, we also observe an inflexion on the 3H curve. The

time interval $(t_2 - t_1)$ is very sensitive to the injected power, the growth rate is lower at lower power (figures 1 and 2).
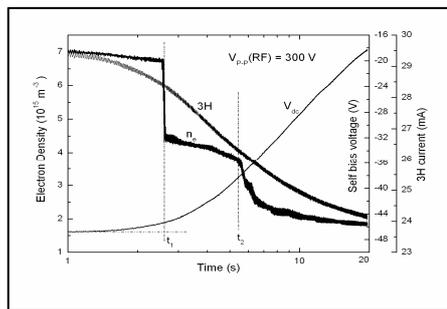
Figure1. Electron density with self bias voltage and current third harmonic at $V_{p-p}(RF) = 300$ V, Pressure = 1.1 mbar and Ar/CH$_4$ = (98 : 2)
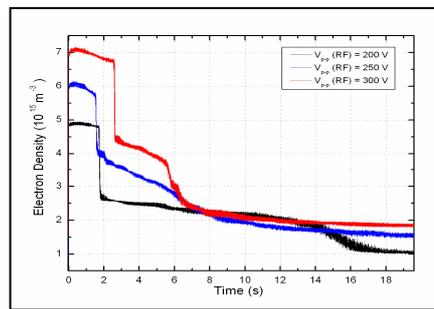
Figure2. Electron density measurements for different $V_{p-p}(RF)$. The other conditions are the same as figure1.

Powders (fig. 3) are collected after several $T_{on} = 20$ s sequences and power of 20 W. The collected powders present a spherical shape. The powders have a radius of around 100 nm with a standard deviation of about 12 nm. This corresponds to a rather monodispersed size distribution (fig.4) and traduces that we have only one powder generation. The cracks observed on some powders are related to the thin gold layer deposited on their surface which is necessary to improve the SEM picture resolution by inhibiting the charge accumulation on the samples.
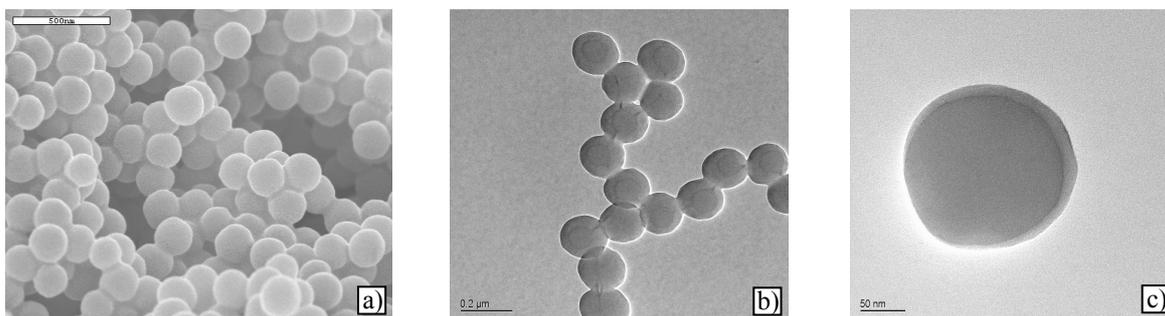
Figure3. SEM (a) and TEM (b, c) pictures of collected powders. (Same conditions as figure1)
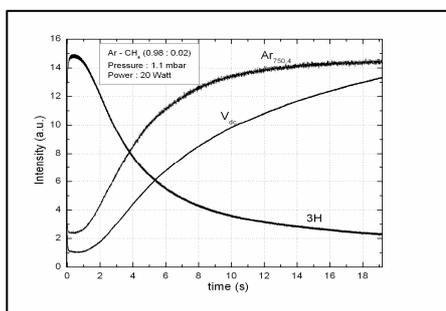
Figure 5 : Ar 750.4 nm line intensity evolution together with V_{dc} and 3H
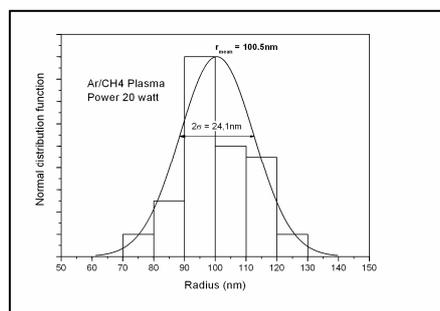
Figure 4 : Dust particle size distribution

Figure 5 shows the time evolution of the Argon 750.4 nm line intensity, relative to the $2p_1 \rightarrow 1s_1$ transition which is assumed to be close to the corona equilibrium, together with the variation of V_{dc} and 3H. In fact, we can note that the $Ar_{750.4}$ line evolution is the same as V_{dc}.

This line is used to estimate the electron temperature evolution ($n_e(t)$). For this purpose the spectrometer was calibrated in terms of energy using a calibrated tungsten ribbon lamp. This enables us to estimate the density of argon excited atoms in the $2p_1$ state. Thus using the corona equilibrium assumption we can deduce the excitation rate coefficient k_{exc} from:

$$\frac{\partial N_i(2p_1)}{\partial t} = n_e N_0(1s_2) k_{exc} - \frac{N_i(2p_1)}{\tau} \tag{2}$$

At steady state, the time derivative tends to zero, and it is easy to estimate k_{exc} and thus the electron temperature using the adequate excitation cross section. The electron temperature values before and after powder formation (1.5 and 2.2 eV) show that this temperature increases due to the electric field exaltation in the plasma bulk, and demonstrate also that $\alpha \to \gamma'$ transition occurs in the discharge, i.e, the discharge shifts from a capacitive behaviour to a resistive one.

IV. CONCLUSION

In this contribution we presented the electrical characterization of a dust forming methane-argon gas mixture RF discharge. The time evolution of the electron density, the self bias and the amplitude of the third harmonic of the discharge current are good tools to detect and determine the different growth phases of the dust particles. We pointed out that there are four growth phases with maybe two distinct agglomeration ones. We also showed how the injected RF power affects the dust formation.

References

[1] A. A. Fridman, L. Boufendi, T. Hbid, B. V. Potapkin, and A. Bouchoule, J. Appl. Phys. **79,** 1303 (1996)

[2] Y. Watanabe, M. Shiratani and K. Koga, plasma Sources Sci. Technol. **11,** A229 (2002)

[3] S. Stoykov, C. Eggs and U. Kortshagen, J. Phys. D : Appl. Phys. **34,** 2160 (2001)

[4] S. Hong, J. Berndt and J. Winter, Plasma Sources Sci. Technol. **12,** 46 (2003)

[5] A. Bouchoule, A. Plain, L. Boufendi, J. P. Blondeau and C. Laure, J. Appl. Phys. **70,** 1991 (1991)

[6] M. heintze and M. Magureanu, J. Appl. Phys. **92,** 2276 (2002)