34th EPS Conference on Plasma Phys. Warsaw, 2 - 6 July 2007 ECA Vol.**31F**, O-3.006 (2007)

Dust particle synthesis in $N_2 - CH_4$ gas mixture capacitively coupled radiofrequency discharge

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ABSTRACT

This paper deals with the study of the growth kinetics of hydrocarbon dust particles in low pressure $N_2 - CH_4$ gas mixture radio frequency discharges. The partial pressure of CH_4 is about 2% of the gas mixture total pressure (0.9 mbar), and the power varies from 20 to 40 W. The initiation and growth of hydrocarbon particles are followed thanks to the measurement of the self bias voltage, the amplitude of the third harmonic of the discharge current, the electron density and the electron temperature. The microwave resonant cavity technique is used to measure the time evolution of the electron density, while the morphology and the size of the collected powders are studied by the means of Transmission and Scanning Electron Microscopy.

INTRODUCTION

In the last two decades, several publications were devoted to the study of powder formation in $N_2 - CH_4$ plasmas. These studies were motivated by the wide range of applications of these plasmas, such as the synthesis of Titan analogue particles [1] or the carbon nitride thin film deposition [2]. Nevertheless, the growth kinetic of hydrocarbon dust particles is not well known. The aim of the present study is to give a few elements which can contribute to a better understanding of the growth steps for this kind of particulates. We have also analysed the influence of a higher methane concentration and of a small amount addition of argon on the growth kinetics of these particles.

EXPERIMENTAL SET-UP AND INVESTIGATION TOOLS

This study was achieved in $N_2 - CH_4$ gas mixture capacitively coupled radio frequency discharge. The experimental setup has already been described in details in previous papers [3-4]. The nitrogen flow rate is 43.5 sccm and the total pressure is kept constant at 0.9 mbar. The methane flow rate and varies from 2 to 4 sccm and the RF power varies from 20 to 40W. The discharge is pulsed by alternating T_{on} and T_{off} in order to control the dust particle size.

Our experimental conditions are close from the ones used to simulate the Titan's analogues in laboratory. Indeed, a capacitively coupled radio frequency discharge allows to keep the dust particles in levitation and permits their growth in the bulk. These characteristics give the opportunity to study the growth and the behaviour of these analogues [1]. This kind of plasmas is also used for carbon nitride thin films deposition [5].

Electron density measurements are carried out using microwave resonant cavity method. This method consists of two antennas placed at 6 cm apart on the lower electrode. The first one is connected to a microwave generator and the second one to an oscilloscope. It is worth to notice that the time resolution of this method depends on the response time of a cavity, which is estimated to be around 500 ns.

Emission spectroscopy is a good tool to estimate the electron temperature. It consists on the measurement of the absolute intensity of the argon 750.4 nm line. Argon is previously introduced in the reactor as trace rare gas. The absolute intensity is achieved by calibrating the spectrometer in terms of energy by a Tungsten ribbon lamp.

EXPERIMENTAL RESULTS

a) Electrical measurements:

Figure (1) shows the variation of electron density (n_e) together with the self bias voltage ($|V_{dc}|$ is represented). One notes that the two curves exhibit the same behaviour. The minima of V_{dc} and n_e (reached at the same time) correspond to the appearance of the second generation of powder in the plasma. This assumption becomes clear when the size distribution of the collected powders is analysed (see figure 2). Indeed, the size distribution can easily be fitted by two normal functions, corresponding to the two existent powder generations. Figure (3) shows the superposition of different electrical parameters on a 1s time range.

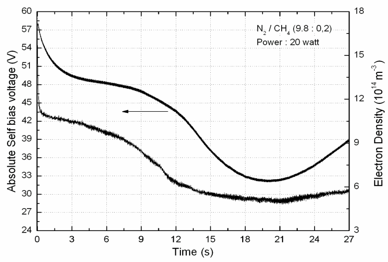


Figure1. Electron density with self bias voltage

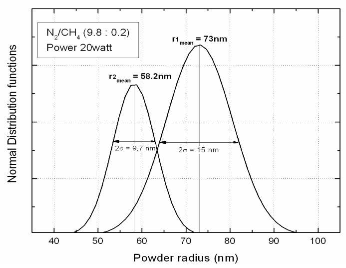


Figure2. Dust particle size distribution

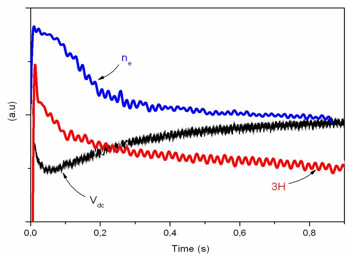


Figure3. Electron density, current 3H and self bias voltage

The electron density exhibits a first drop from ignition to 300 ms. The decrease of n_e induces the decrease of the current third harmonic and the self bias voltage. Figure (4) shows the Argon 750.4 nm line intensity evolution used to estimate the electron temperature. We founded that the electron temperature is around 1.1 eV when the plasma starts and reaches a maximum value of about 1.4 eV after 20 s (the minima of n_e and V_{dc} are achieved at the same time). The analysis of the results allows us to give prominence to the fact that the electron density drop (associated to the coagulation phase) is not as strong as in argon-silane chemistry [6]. This can be attributed to that in the same conditions, the electron density is lower in molecular gases (nitrogen) than in atomic gases (argon). The electron temperature is twice higher at the ignition in argon plasmas. Thus, the charge carried by powders in $N_2 - CH_4$ plasmas is less than the one carried by the same size powders in $Ar - CH_4$ plasmas. Moreover, the coagulation occurs faster than in argon/methane dilution, which suggests that the primary clusters are instantaneously formed in $N_2 - CH_4$ plasma, while this step takes few seconds before occurring in $Ar - CH_4$. One can say that the dust formation acetylene way is not the most important in $N_2 - CH_4$.

b) ***Influence of methane flow rate variation and addition of argon***

In this section, the influence of the methane concentration and the argon addition on the growth kinetics of hydrocarbon dust particles in methane/nitrogen plasma is studied.

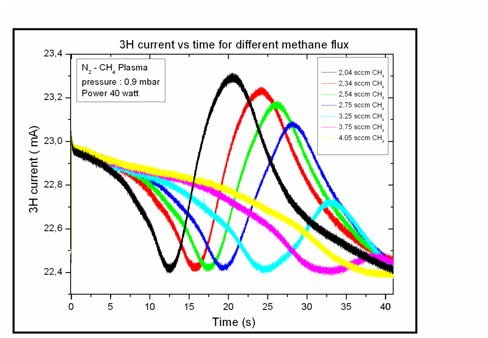


Figure5. Variation of the current third harmonic versus methane flow rate

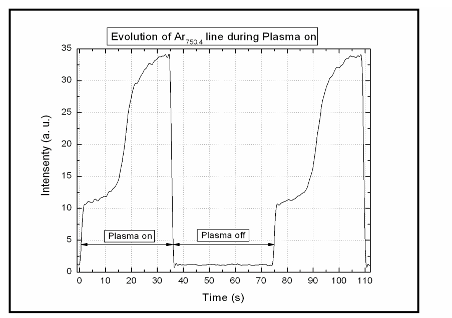
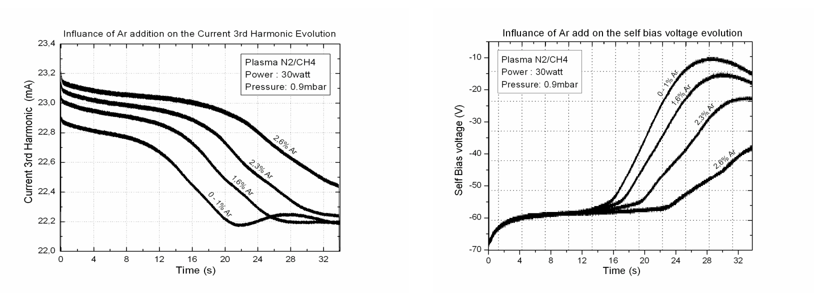


Figure4. Ar 750.4 line intensity evolution

Figure (5) shows the time-evolution of the current 3H for different methane gas flow rates. It is known that the current 3H decrease is attributed to the electron loss on the powders. 3H minimum is reached when the higher size powders is achieved, i.e., because in rective plasma, the dust growth ends by molecular accretion which do not modify the dust density. When the current third harmonic increases again, the bigger size powders are pushed out the plasma and an other powder generation can start to grow in the bulk plasma. The fundamental observation is that at fixed pressure and power, the growth kinetics is got slowed down when the methane flow rate is increased.



Figur6. Current third harmonic (left) and self bias voltage (right)

Figure (6) shows the time evolution of the current 3H and V_{dc} with different argon rates. The addition of a small amount of argon leads to a small variation of the electron density, highly visible on the 3H curves which is very sensitive to the electron density variation. The growth kinetics is slowed down when the argon rate is increased. A scrupulous observation of figures (5) and (6) allows to deduce that the methane and argon addition influences is on the last stage of the powder formation which lasts longer.

CONCLUSION

In this paper, the hydrocarbon dust formation in capacitively coupled radio frequency discharge in $N_2 - CH_4$ mixtures has been studied. The dust formation is instantaneously induced in our plasma in contrast with $Ar - CH_4$ mixture. We deduced that the dust formation acetylene way is not the most important. We have also pointed out that the addition of small amount of methane and argon slows down the accretion phase, but do not influence (a priori) the accumulation and coagulation phases.

References

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