CYCLING INSTABILITIES IN A GAS AGGREGATION CLUSTER SOURCE USED FOR PLASMA POLYMER NANOPARTICLE FABRICATION

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Abstract

This work investigates plasma instabilities occurring in a Gas Aggregation Cluster Source (GAS) and correlates them with the formation and growth of hydrocarbon nanoparticles (NPs). For this aim, special configuration of the GAS was employed, which allows for simultaneous measurements of the discharge voltage, the optical emission (OES) and the mass spectra (MS). Cycling instabilities with a period of 80 s were detected in the deposition rate which correlated with the changes in the discharge voltage, the intensity of the plasma emission and the concentration of hydrocarbon species.

1. INTRODUCTION

Dusty plasmas or complex plasmas have been explored for several decades [1-4]. The formation of nanoparticles (NPs) have been observed in the discharges ignited at a pressure of tens of Pa in a variety of gas mixtures including silane, hydrocarbons and fluorocarbons [5-7] and using different types of reactors [8-10]. Deeper investigation demonstrated that NPs may form and disappear in a cycling regime, a phenomenon called void instabilities. A balance of forces acting on growing NPs was brought forward to explain such collective behavior [11]. It was recognized that small negatively charged NPs levitate in the discharge region due to the balance of the forces acting on them. As soon as the NPs reach the critical size, the balance is violated and they are pushed out of the discharge. The process was found to be periodical as was confirmed by the temporal FTIR, mass-spectrometry and OES measurements [12-14]. The results obtained by means of different constructions of dusty plasma reactors showed the strong dependence of a cycle period on the reactor form, size and experimental parameters. The nature of such behavior has not been fully explained yet.

Recently, the use of gas aggregation cluster sources (GAS) has been adapted for the production of micro- and nanoparticles [15]. A typical GAS consists of a water-cooled vacuum chamber which is equipped by an r.f. electrode or magnetron at one side and with a small exit orifice at the opposite side. The operational conditions inside the GAS can be optimized to force the formation of nanoparticles. The co-axial gas flow is deliberately created in the GAS to drag the nanoparticles away from the discharge, through the orifice and into another vacuum chamber where they can be collected on solid substrates. The effectiveness of GASes for the preparation of plasma polymer particles was demonstrated using a number of volatile precursors such as *n*-hexane and hexamethyldisiloxane, or by the r.f. magnetron sputtering of polymeric targets made of nylon and poly(tetrafluoroethylene) [15-17]. However, the diagnostics of the processes occurring inside a GAS has been attempted only recently [18] and the formation of voids has never been reported. The aim of the current work is to find the conditions for the void formation during the formation and growth of hydrocarbon plasma polymer nanoparticles in the GAS and to investigate these processes by in situ diagnostic methods.

2. EXPERIMENTAL PART

The diagnostic model of a GAS was used for the fabrication of hydrocarbon nanoparticles (see **Figure 1)**. A 3-inch r.f. electrode was powered by a generator (Dressler Caesar, 13.56 MHz). The distance between the electrode and exit orifice (diameter 2 mm) was 16 cm. The GAS was attached to a deposition chamber where quartz crystal microbalance (QCM) and a loadlock system with a substrate-holder were mounted. The aggregation chamber of the GAS was equipped with diagnostic ports for in situ analysis. The bottom port was connected through a 100 um orifice to a mass spectrometer (Hiden Analytical, HAL 301 RC). The top port was used for monitoring the aggregation zone by photo camera or by optical emission spectroscopy (Avantes AvaSpec-3648-2-USB2). The GAS was preliminary pumped by rotary and diffusion pumps down to 10^{-4} Pa. The 4.6 % mixture of n-hexane (Sigma Aldrich) with argon (purity 99.99 %) was used for the production of nanoparticles under the total pressure of 46.3 Pa in the GAS. The working pressure in the deposition chamber was set at 2 Pa. All experiments were performed using the constant power of 50 W. The size and shape of NPs were characterized by scanning electron microscopy (SEM, Tescan Mira II).

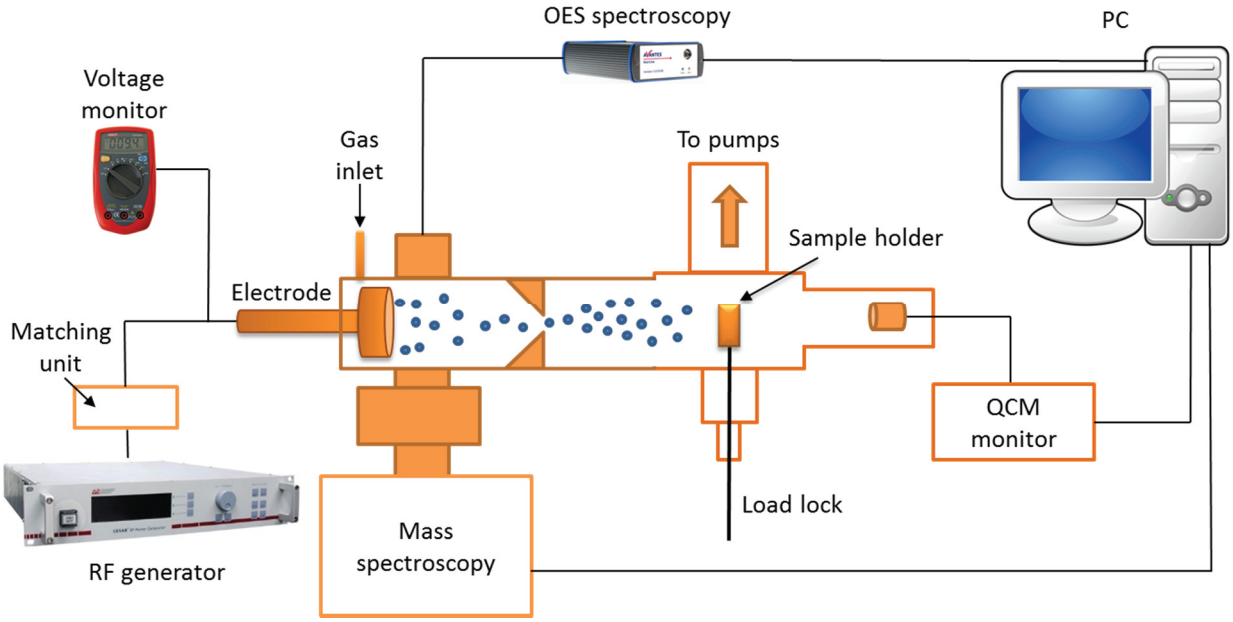

Figure 1 Simplified scheme of the experimental set-up

3. RESULTS AND DISCUSSION

For the diagnostic of plasma instabilities inside the GAS, the temporal dependences of the bias voltage and the mass deposition rate were measured (**Figure 2a**). The periodic character of both graphs was detected which is typical for the dusty plasmas [19,20]. The analysis of dependences revealed the oscillation period equal to 80 s. Moreover, the position of the maxima of the deposition rate was shifted with respect to the maxima of the bias voltage. Details of this phase shift can be seen in **Figure 2b**. The maxima of the deposition rate correspond to the situation when plasma is rich with the nanoparticles and it is accompanied by the lowest value of the bias voltage. The decrease of the number of the nanoparticles and the start of the void formation inside the discharge are associated with an evident growth of the bias voltage and with a decrease of the deposition rate. The top position of the bias voltage corresponds to the moment when the dusty particles are practically absent within the plasma. Later on, a new portion of the nanoparticles starts to form, the bias voltage decreases and a new cycle repeats.

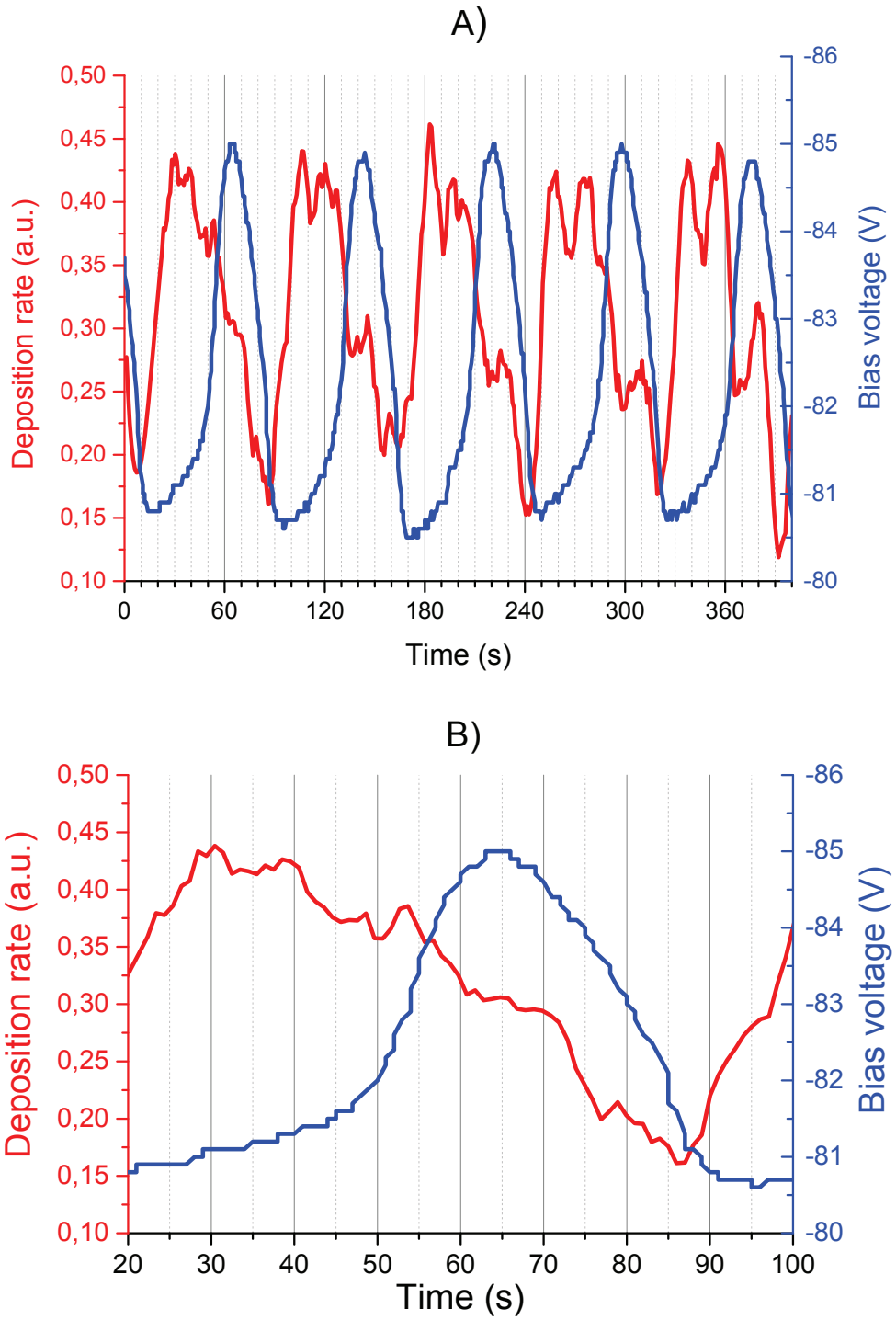

Figure 2 Time evolution of the nanoparticle deposition rate and the bias voltage during the GAS operation (A) and details of one cycle with snapshots made every 5 s (B)

The corresponding periodic instabilities were also revealed in the temporal dependences of the selected peaks in the mass spectra; see **Figure 3**. Distinct oscillations can be seen for the species with m/z = 86 which correspond to the *n*-hexane molecules. A decrease of the signal is attributed to the consumption of the precursor molecules in plasma chemical transformations during the nanoparticle growth. The reference spectrum of argon $_{36}Ar^{+}$ demonstrates the different behavior without any cycling (**Figure 3b**).

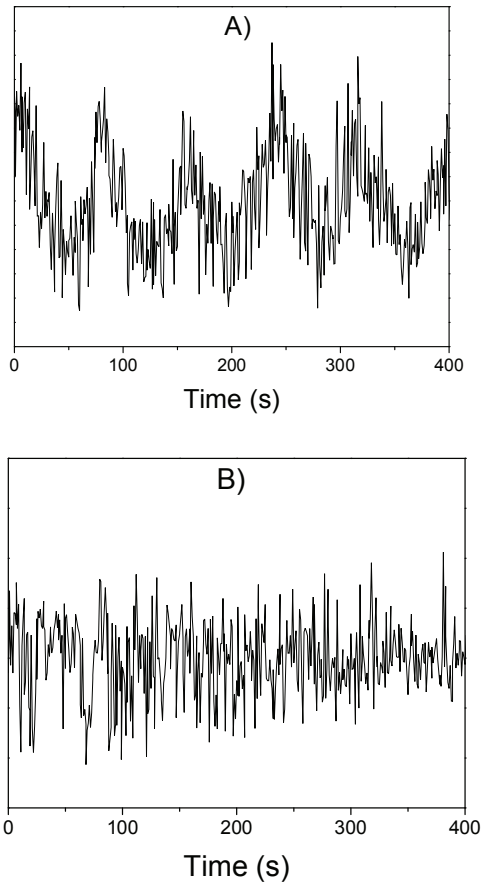

Figure 3 Time dependences of the selected peaks in the mass spectra: a) for mass 86 (C_6H_{14} precursor); b) for mass 36 (Ar)

In addition, the optical emission spectra of the discharge were obtained. The time-resolved dependence of the intensity of the Ar line (707 nm) normalized to the maximum value exhibits the same periodical behavior; see **Figure 4**. According to the previous research, the intensity of the emitted light increases during the formation of nanoparticles due to an increase of the electron energy associated with a decrease of the plasma density [20]. As soon as the void starts to grow, the sharp reduction of the intensity is observed.

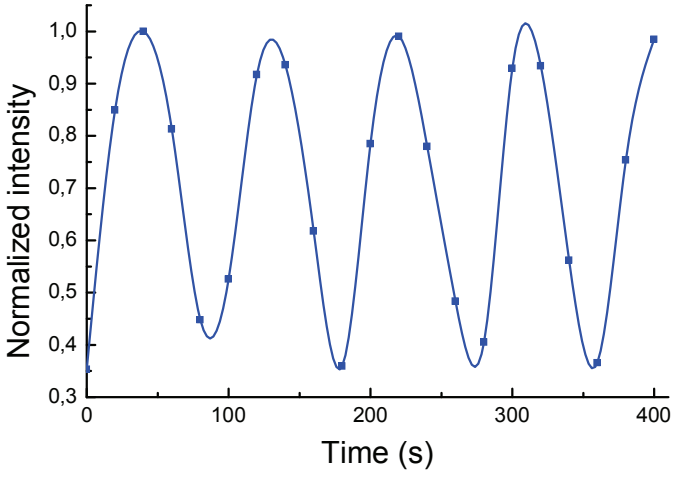

Figure 4 The time evolution of the maximal intensity of the Ar (707 nm) spectral line

The morphology of the particles was analyzed by scanning electron microscopy. The sub monolayer of the CH NPs was deposited on the polished Si wafers and covered by a thin Pt layer to achieve better image contrast. The view of the particles is presented on **Figure 5**. It is worth noting that the nanoparticles retain the spherical symmetry with a highly developed surface morphology, often referred to as the cauliflower structure. The nanoparticles show narrow dispersity with the mean size of 320 ± 23 nm.

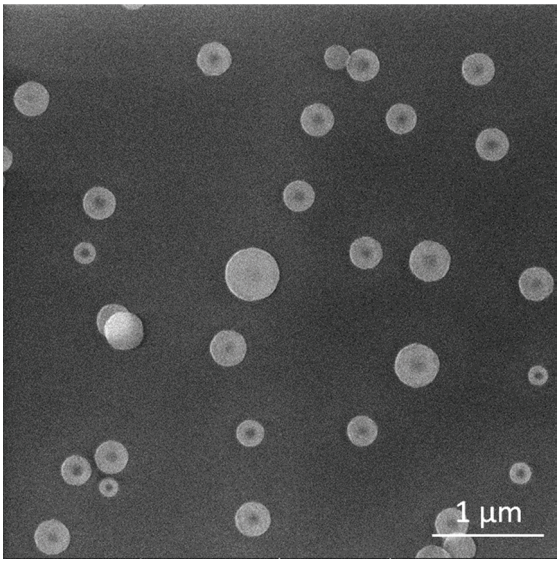

Figure 5 SEM image of hydrocarbon nanoparticles produced by GAS

4. CONCLUSION

The processes of the formation and growth of hydrocarbon nanoparticles inside the gas aggregation cluster source were investigated by means of different diagnostic methods. The temporal dependences of deposition rate, bias voltage, mass spectra and OES spectra show the cycling instabilities typical for dusty plasma. The formation of the particle cloud followed by the formation of the void was clearly observed. Narrowly-dispersed plasma polymer nanoparticles with the mean size of 320 nm were prepared.

ACKNOWLEDGEMENTS

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