Dynamics of a growing dust particle cloud in a direct-current argon sputtering glow discharge

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The growth of nanoparticles from the sputtering of a tungsten cathode and their transport are investigated in a direct-current low pressure argon glow discharge. The dust particle size distribution and the dust particle concentration are measured by light extinction spectrometry. Results are correlated to previous electron microscopy measurements and to laser light scattering of a vertical laser light sheet. Light extinction spectrometry reveals a growth by agglomeration and the appearance of a new dust particle generation. Laser light scattering shows that, while growing, the dust cloud is pushed towards the discharge edges and the anode.

1. Introduction

Dusty or complex plasmas are partially ionised gas which contain solid dust particles. These particles acquire an electric charge due to their interactions with the surrounding ions and electrons. In laboratory experiments, particles can be either injected or grown directly inside the plasma. For example, they can be produced in astrophysical plasmas, in industrial plasma processing reactors, in tokamaks from the physical and chemical erosion of the wall, etc.

In this paper, the dynamics of a growing tungsten nanoparticle cloud is investigated. The particle are produced from the sputtering of a tungsten cathode in a direct-current (DC) low pressure argon glow discharge. The dust particle size distribution and the dust particle concentration are measured by light extinction spectrometry (LES) at different height above the anode. Electron microscopy measurements and Raman spectroscopy of the nanoparticles collected at the centre of the anode are also performed in order to study their shape and composition. Laser light scattering at 90° of a vertical laser light sheet passing through the plasma is used to investigate the dynamics of the dust cloud. LES reveals a growth by agglomeration and the appearance of a new dust particle generation. Laser light scattering shows that, while growing, the dust cloud is pushed towards the discharge edges and the anode.

2. Experiment

2.1. Discharge set-up

A detailed description of the experimental set-up is given in Ref.[1]. The tungsten nanoparticles are grown in a dc argon glow discharge initiated between a tungsten cathode of 10 cm in diameter and a stainless-steal grounded anode. The inter-electrode distance is 10 cm. Two glass half-cylinders are used to confine the plasma. A 1 cm gap is kept between them for optical studies (see Fig.1). A static argon pressure of 0.6 mbar (no gas flow) is set during the experiments. The electrode assembly is contained in a cylindrical vacuum chamber of 30 cm diameter and 40 cm length. An oil diffusion pump achieves a base pressure $\leq 10^{-6}$ mbar.

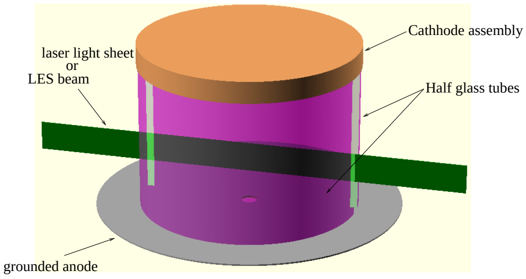

Fig. 1: Schematic of the cathode assembly

A regulated power supply is used to bias the cathode. The discharge current density is kept at a constant value (0.53 mA·cm^{-2}). The current variations are less than 0.05 %. The discharge voltage is the free parameter whose time evolution is acquired during the discharge. Under the chosen operating conditions, the cathode is sputtered and tungsten nanoparticles are grown.

2.2. Ex-situ diagnostics

The anode disc has a 1.6 cm diameter hole at the centre through which the tungsten nanoparticles produced during the discharge are collected on stainless steel foils. Dust particle size distributions (PSD) can be recovered from ex-situ using a scanning electron microscope analysis. Two methods of collection are used [2]:

- (i) Substrates are exposed to the plasma only during a given time interval.
- (ii) Substrate sees the end of the discharge.

Dust particle are also transferred from the stainless steal substrate to transmission electron microscopy grid in order to performed high-angle annular dark-field imaging (HAADF) with a scanning transmission microscope (STEM). This technique, being highly sensitive to variations in the atomic number of atoms in analysed samples, was used to check the tungsten content of the nanoparticles.

In order to determine if the nanoparticles are oxidised or not, post-mortem Raman spectroscopy is also performed directly on the stainless steel samples covered with dust particles. Tungsten oxides are indeed known to exhibit optical Raman active bending and stretching modes in the ranges 100-300 cm^{-1} and 700-800 cm^{-1}, respectively [3] whereas pure tungsten does not display any optical Raman active mode.

2.3. Laser light scattering

A 2 cm height vertical laser light sheet (40 mW, wavelength $\lambda = 532$ nm) is passing through the electrode assembly in the gap between the half-cylinders (see Fig.1). The scattered light by the dust particles is recorded at 90° by a CCD camera. A low frame rate of 1 frame per second and a long exposure time of 0.5 s are used to overcome the weakness of the scattering signal. The position of the laser sheet between the electrode can be chosen at the time of the experiment. A bandpass filter centred on the laser wavelength is placed in front of the camera in order to minimise the recorded plasma light.

2.4. Light extinction spectrometry

LES consists in passing through the cloud of particles to be analysed, a collimated and polychromatic beam with spectral intensity $I_0(\lambda_i)$ and wavelengths λ_i. Then, the directly transmitted spectral intensity $I(\lambda_i)$ is collected and directed towards a spectrometer via an optical optical system with a small acceptance angle. If the collection of multiple scattered photons is negligible, the beam transmission T_{λ_i} is given by:

$$T_{\lambda_i} = \frac{I(\lambda_i)}{I_0(\lambda_i)} = \exp(-\tau(\lambda_i) \cdot L) \qquad (1)$$

where L is the probing distance and $\tau(\lambda_i)$ is the particle system turbidity. The turbidity is the product of the particle number concentration N and the mean extinction cross section of the particles, which are illuminated by the probing beam. The mean extinction cross section is an integral quantity depending on the properties of each particle and its statistical weight in the particulate medium. From the measured transmission spectra, it is thus possible to recover the dust particle concentration and the dust particle size distribution. Details about the inversion procedure can be found in [4, 5].

3. Results

3.1 Ex-situ measurements

Scanning electron microscopy results have been described in details in previous articles [1, 2]. Here is a quick outline of the main results:

- Dust nanoparticles are pushed towards the anode located at the bottom of the discharge setup and can be detrapped and fell on it.
- The latter the substrate exposed to the plasma, the bigger the particle on it.
- Small particles (with a mean diameter ~30 nm) are always observed on the substrate when the dischage is switch off (method (ii)). This results indicated a constant nucleation and growth of particles in the upper part of the discharge (cathode side).

HAADF-STEM sudies of particles collected after a 300 s plasma indicates that the nanoparticles are spheroids, mainly composed of tungsten crystallites (2-4 nm). Weak tungsten oxide signatures are also observed by Raman spectroscopy. In order to check if nanoparticles are weakly oxidized, they have been heated under an oxygen containing atmosphere. The growth of tungsten oxide bending and stretching modes is observed for temperature higher than 700°C. Final intensities are multiplied by a factor of $\simeq 25$ showing that the weak bands, observed at room temperature are due to surface oxide, probably formed during the venting of the chamber, after experiments. Therefore, we can conclude that the nanoparticles produced in our conditions are mainly composed of W and the optical properties of pure tungsten have been used for LES measurements .

3.2 Laser light scattering

In a previous study, laser light scattering analyses, just above the anode revealed that the dust particle cloud is compressed and pushed towards the anode [2]. For a better understanding of the dynamics of the growing dust particle cloud, many experiments with different height of the laser sheet, above the anode have been performed. In every experiment, no dust particle could be detected by laser light scattering before 30 s after plasma ignition. In Fig.2(a), snapshots of the video of the scattered light are shown. The lower edge is positioned 2.4 cm above the anode. As can be seen, the scattered light intensity increases with time until the dust cloud is pushed down and toward the side of the discharge and an apparently "dust-free" zone is created in the discharge (no dust particle can be detected by laser light scattering). In Fig.2, this effect is particularly well seen at t=210 s in which the top edge of the dust particle cloud is concave. Note that this behaviour is observed at all investigated height between the electrodes. Measurements performed close to the cathode reveals that the dust cloud is pushed by the hemispherical expansion of the negative glow from the cathode center. In Fig.2(b), the distance of the upper edge of the dust particle cloud is plotted as a function of time. As can be seen, the maximum height of the dust cloud edge is ~6.5 cm above the anode at t~30 s after plasma ignition. Soon after the dust particle cloud can be detected, it starts to be pushed toward the anode and the edge of the discharge. For ~100 s the movement of the dust cloud is quite slow and the height variation of the upper edge is ~1 cm. Then, in ~200 s the upper edge position falls from ~5.5 cm to less than 1 cm, meaning that a major part of the discharge gap seems free of dust. It is however not the case as our previous studies have shown that small dust particle (hardly detectable by laser light scattering) are growing in the region [2].

3.3 Light extinction spectrometry

Light extinction spectrometry measurements were performed a few centimeters above the anode. In Fig.3(a), the evolution of the transmittance 2.8 cm above the anode as a function of time for wavelength in the range 220-850 nm is presented. As it can be seen, the short wavelength transmittance is more affected by the presence of the growing tungsten nanoparticles while a decrease in the transmittance at long wavelengths is hardly noticeable as expected for nanometre size particles.

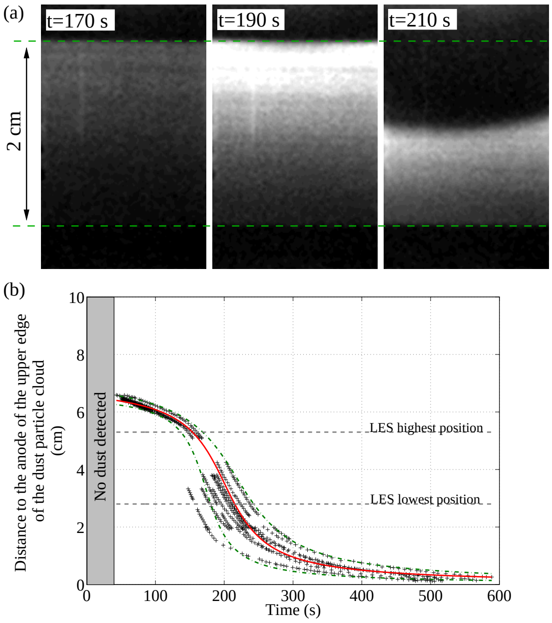

Fig. 2: (a) Snapshots of the video of the scattered laser light at different time after plasma ignition. The dashed green lines show the upper and lower edges of the vertical laser sheet. The lower edge of the laser sheet was 2.4 cm above the anode. (b) Distance of the upper edge of the dust particle cloud (1^{st} generation) to the anode on the discharge axis as a function of time extracted from Laser light scattering video data. The data are accumulated over 23 experiments. The red line represents the mean evolution position of the upper edge of the dust cloud. The dashed green lines are the errorbars at 2σ.

In Fig.3(b) and (c), the recovered evolution of the dust particle mean diameter and the dust particle concentration are presented. Before 50 s no data could be extracted from the transmittance spectra. From t=50 s, particles with a mean diameter ~30 nm and a concentration ~10^{14} m^{-3} can be detected. On the transmission spectra, one can see that from plasma ignition, the transmittance has slightly decreased. This effect is mostly seen at short wavelengths. From t~120 s, the dust concentration starts to decrease rapidly while the dust diameter is increasing. On the transmission spectrum, one can see that it correspond to a decrease of the transmittance at all wavelengths. This is a clear signature of the agglomeration process. Slightly before 200 s, the mean dust diameter saturates and the dust concentration decreases now at very slow pace. At ~220 s, the transmittance reaches its first minima at all wavelength. However, the mean dust diameter and the dust concentration do not seem to be very affected. From laser light scattering measurements, it can be deduced that this moment corresponds to the edge of the top cloud,

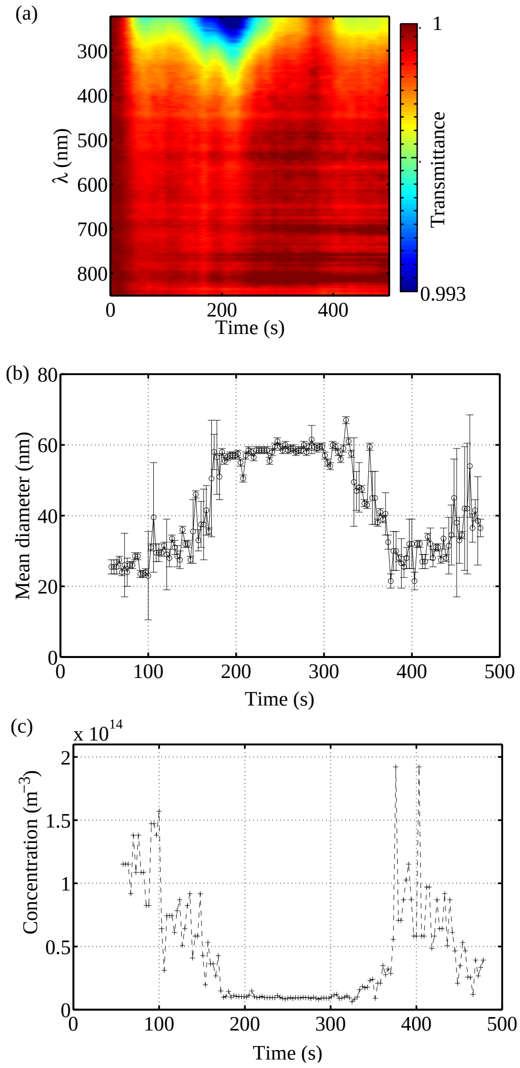

Fig. 3: (a) Evolution of the transmitance at different wavelength as a function of time, 2.8 cm above the anode for a 500 s discharge. (b) Recovered evolution of the particle mean diameter. (c) Recovered evolution of the dust particle number concentration.

being at the height of the LES light beam. Two reasons can explain the lack of change in the diameter and concentration curves: (i) it was shown that small particles are constantly growing in the discharge and consequently the “empty region” observed by laser light scattering is filled by them (ii) LES is more sensitive to large particles. Therefore, if two generations of nanoparticles are present in the beam, LES will mainly detect large ones, belonging to the first generation. From ∼350 s, the dust concentration increases again and the dust diameter decreases again. On the transmittance spectrum, it corresponds to a re-decrease of the transmittance. This observation is in accordance with our former observation [2]: the large particles are expelled from the plasma and new nanoparticles are synthesized in their place. They grow above the main dust cloud, in a region were nucleation can take place again from sputtered atoms. This behaviour is similar to that observed in radio-frequency discharges were a ”void” usually appears in the plasma center, in which new dust particles are grown [6, 7] .

4. Discussion and Conclusion

In this article, the growth of nanoparticles from the sputtering of a tungsten cathode as well as their transport were investigated in DC low pressure argon glow discharges. Laser light scattering of a vertical laser sheet, set above the anode showed that the dust cloud was pushed towards the edge of the discharge and the anode. In addition, the evolution of the dust particle size distribution and concentration were studied by light extinction spectrometry. This diagnostic, based on the polychromatic analysis of the transmited light through a dust cloud has revealed a phase of growth by agglomeration, followed by the appearance of a second nanoparticle generation. Results have also shown that the latter appeared in the space freed by the first nanoparticle generation.

5. References

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