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Forces applied to nanoparticles in magnetron discharges and the resulting size segregation

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ABSTRACT

Two-dimensional measurements of magnetron discharge plasma parameters are used to calculate the forces applied to an isolated nanoparticle in conditions where nanoparticles are produced from cathode sputtering. Plasma spatial inhomogeneities, which are specific to magnetron discharges also induce inhomogeneities in the charging mechanism and applied forces. It is shown that the nanoparticle transport is is due to electric, thermophoretic and ion drag forces, and that the dominant one proportional to the nanoparticle size varies according to position. For a given plasma, these spatial differences explain the segregation of size in the nanoparticle deposits, which are observed inside the device.

I. INTRODUCTION

The presence of nanoparticles (NPs) in plasmas is strongly dependent on discharge conditions (geometry, gas pressure and temperature, magnetic and electric field configurations, discharge current or voltage). These conditions are also at the origin of the plasma parameters necessary for their formation, charging, heating and transport, and their characteristics such as morphology, size, crystallinity that make the diversity of their applications. The later extend from electronics,[1] optics,[2] catalysis[3] to biology as nanoscale materials have improved properties compared to those of bulk materials. Studies on the dust nucleation and growth have been made extensively in various sources of low temperature reactive plasmas such as radio-frequency (RF)[4-6] and direct-current (DC) sources,[7-8] in presence of magnetic fields in gas-aggregation systems based on magnetron discharges (MS-GAS)[9,10] or in conventional magnetron discharges,[11,12] in microwave plasmas combined with DC plasmas,[13] electron cyclotron resonance (ECR) plasmas[14] and strongly magnetized RF plasmas.[15] The production of dust has also been investigated in tokamaks. Formation mechanisms from plasma-wall interaction have been identified when plasma facing components are made of graphite[16,17] as well as metal such as tungsten[18] or molybdenum.[19] Similarities between the nucleation mechanisms in laboratory plasmas and in the coldest plasma regions of tokamaks have also been established.[16,20]

During their growth, dust particles get charged due to negative and positive plasma particles fluxes on their surface. The electron mobility being the largest, they acquire a net negative charge. In addition, the growth and charging mechanisms depend on the position, trapping or motion and in turn, the forces that govern the dynamics of NPs depend on their size and density, and ~~the~~ local plasma parameters. The main forces acting on their transport are the electrostatic force due to plasma and sheath electric fields,[21,22] forces due to momentum exchange with other particles such as neutral and ion drag forces,[21-25] attractive forces due to ion streaming,[26,] thermophoretic forces due to gas temperature gradients,[27,28] and the gravitational force. Many experiments have been dedicated to the dust cloud dynamics using most commonly CCD cameras, Mie-scattering ellipsometry,[29,30] or a simplified optical method based on laser scattering-extinction[4,31] and the powerful diagnostic of light extinction spectroscopy providing the evolution of the NP size distribution and absolute concentration for a given position.[32] On the other hand, in MS-GAS systems where a magnetron cathode is used as sputtering source for nucleation, the NP transport is essentially studied after an orifice separating the plasma chamber from the deposition chamber of substantially lower pressure. This technique through the buffer gas expansion is at the origin of variations in NP velocity and segregation into the deposition chamber.[33,34] Velocities are measured using the electrostatic deflection technique,[35] or a quadrupole mass filter combined with a retarding filed analyzer.[36] Overall, studying the transport of NPs is necessary to understand the formation characteristics and deposition mechanisms.

In this paper, we present for the first time a study on the forces applied to NPs which are produced from cathode sputtering in conventional magnetron discharges. During plasma operation, the location of their deposition varies according to their size. Therefore, our goal is to show the importance of some forces, their variation as a function of position in the plasma and the resulting effects on the dust motion. In a recent paper, we have presented two dimensional (2D) measurements of the magnetic field in our magnetron system as well as well as 2D measurements of plasma parameters in conditions where tungsten NPs are produced.[37] In this paper, we show that these parameters completed by others have allowed to integrate the analytical expressions of forces applied in a first approach, to an isolated NP. For a given plasma, 2D mappings of the main forces will be presented and will show that there can be different trajectories in the NP transport leading to a size segregation inside the device, in agreement with our experimental observations.

The experimental set up will be presented in Sec. II with a description of the diagnostics used for plasma parameter measurements. Examples of tungsten NPs of different sizes, collected in various locations will also be presented. In Sec. III, 2D mappings of the plasma parameters and forces applied to an isolated NP will be presented. Sec. IV is dedicated to the forces balance and the resulting deposit locations. Results will be discussed. A conclusion will be given Sec. V.

II. EXPERIMENTAL SETUP AND MEASUREMENTS

A. Experimental setup

The device is a stainless-steel cylinder of 40 cm in length and 30 cm in diameter. The ionization source is an unbalanced planar magnetron system (mcse-ROBEKO) schematized in the upper part of Fig. 1 and previously described.[37] The cathode arranged at the top of the device is a tungsten disc of 7.6 cm in diameter and 0.3 cm in width. It is equipped with permanent magnets and a water flow system that ensures its cooling during discharges. A grounded guard ring (anode) of ~ 7.4 cm inner diameter, 2 cm in width and 1 cm in height is set under the cathode at a distance of ~ 0.2 cm and all around. A grounded stainless-steel disc of 15 cm in diameter (anode plate) is placed parallel to the cathode at 10 cm.

A glass cylinder of ~ 12 cm inner diameter and 12 cm long was introduced to trap the nanoparticles produced from cathode sputtering. It was cut vertically into two half cylinders that were settled around the magnetron system. In a first step, they were separated by ~ 1.5 cm on each side to allow the introduction of a Langmuir probe. In a second step, one of these glass pieces was cut into two parts in order to use the Laser Induced Fluorescence (LIF) diagnostic (lower part of Fig. 1). With this setup, a laser beam can be introduced into the plasma parallel to the cathode. LIF signals can be detected in several positions through the free spaces let between the glass pieces.

The base vacuum is maintained at < 10^{-6} mbar using a turbo molecular pump. Discharges are produced in argon at P_{ar} = 30 Pa pressure and a slow 5 sccm (standard cubic centimeters per minute) flow rate, the gas inlet being located at the top of the device. The discharge current is maintained constant at 0.3 A using a DC current-regulated power supply (Glassman HV, 1A-1kV) meanwhile the discharge voltage self-adjusts to around - 200 V.

B. Diagnostics and procedures:

Magnetic field measurements were performed in the vertical plane (r, z). For this, a small calibrated Hall probe (Hirst Magnetics GM08) was used into the device without plasma. The probe was a gallium arsenide semiconductor plate of 0.1cm × 0.1cm embedded in a thin long resin stripe linked to a gaussmeter (GM08-HIRST). It was moved radially every 0.2 cm from r= - 5 to r = 5 cm, r = 0 cm being the discharge axis position. These measurements were repeated vertically every 0.5 cm from z = 0.4 cm (~ cathode surface) to z = 10 cm. A matlab program was used to reconstruct the corresponding B field values and lines. The latter are schematized in the upper part of Fig. 1 in between the cathode and anode plate. Details are given in reference "Chami et al. (2020)".[37]

A homemade Langmuir cylindrical probe (LP) consisting of a 1 cm long tungsten tip and 62.5 μm radius was used to measure spatial variations of the electron density n_e, temperature T_e and plasma potential V_p. The probe axis was moved radially in between the two pieces of glass tubes from r = -2 to r = 6 cm. These measurements were repeated every centimeter from z = 2 to z = 9 cm. To avoid the LP contamination, the plasma duration was first limited to the time necessary for cleaning by electron bombardment (several seconds, several times) then to the time necessary to acquire three LP characteristics (I-V) in ~ 15 s. Several series of I-V curves were obtained for a given z and the probe tip was changed at each z position. LP characteristics were recorded with a driver (Princeton Instruments) and data were processed using a matlab program. After subtracting the ion current, n_e and V_p were found from the first derivative of the LP characteristic and T_e from the logarithm of the probe current.

The LIF diagnostic allowed to find spatial variations of argon temperature. The laser source was a single-mode tuneable diode laser (Toptica Photonics, Sys DL 100, 30 mW) operating at wavelengths centred at λ_0 = 772.38 nm. The fluorescence signal was collected with a photomultiplier tube (PM) equipped with a camera lens and an interference filter. The signal was sent to a lock-in amplifier (EG&G 5210 model, Princeton Applied Physics) working with a reference frequency (~1.6 kHz) given by a chopper (scheme in the lower part of Fig. 1). The laser wavelength was scanned through a slow imposed ramp (~ 25 s) compared to the integration time of the lock-in amplifier (100 ms), this providing the LIF signal directly. A part of the incident laser beam was sent to a Fabry-Perot cavity used to calibrate the laser frequency scan. Another part was sent to an Ar discharge cell where its absorption provided the reference λ_0 at room temperature. The four signals were recorded by an oscilloscope (LeCroy, Wave Runner, 1GHz) and then processed by computer. For measurements, the incident laser beam was displaced every centimeter from z = 1 to 5 cm. The FIL emission was detected at 90° of the incident beam direction and along the plasma axis. In a second step, the detection system was moved by $\theta \sim 8°$ from the perpendicular direction of the laser beam to record signals under the erosion ring of the cathode also called "racetrack" (average position at r = 2.2 cm). LIF signals were also recorded at r = 6 cm in the laser forward direction but under a small angle to avoid receiving the direct beam.

C. Nanoparticle sampling

In the presented conditions, NPs can be grown in the plasma volume from sputtered tungsten atoms coming from the cathode racetrack. During formation (not in the scope of this paper), NPs were mostly transported towards the guard ring and a smaller part towards the anode plate. In the latter case, they were deposited on grounded stainless-steel polished substrates (1cmx1cm) that can be pushed one after the other under a hole drilled in the anode plate center. These substrates were directly investigated with scanning electron microscopy (SEM). In order to produce enough NPs and to see enough on substrates, several plasmas of same duration were produced successively with a stopping time of 15 min necessary to reach a vacuum < 10^{-6} mbar.

SEM image of Fig. 2(a) shows NPs found in the center of a substrate after 10 plasmas of 200 s. The average size is around 30 nm.[38] Figure 2(b) shows NPs synthetized over the same plasmas but deposited on the guard ring. The average size is around 10 nm. Figure 2(c) shows the guard ring from which they were extracted using a pipette with ethanol. They were then transferred to a substrate similar to other. Notice that the surface of the guard ring is covered by a fairly homogeneous layer of NPs (black layer). Understanding differences of sizes as a function of position of NP deposits will be the topic of sections IV and V.

III. PLASMA PARAMETERS

A. Magnetic field measurements

The complete 2D mapping of magnetic field strengths and lines was already published.[37] Figure 3 shows the decrease of the magnetic field B in Log scale along the discharge axis (r = 0 cm) under the racetrack average position (r = 2.2 cm) and under the guard ring (r = 5 cm). The maximum reached at the cathode center is B = 860 G. The magnetic null point is at (r, z) = (0 cm, 3.4 cm). In the sheath-presheath region of the anode plate (z ~ 9 cm) values are smaller than 10 G.

Usually in magnetron discharges, ions are not magnetized especially when the atomic mass of gas is large and more readily, when the magnetic field is getting smaller and smaller in the background plasma. In the complex magnetic configuration of the cathode sheath-presheath, electrons experience an ExB drift driving a Hall current just above the cathode racetrack.[39-41] In the background plasma, since the decrease of B is almost exponential, a rough approximation consists in considering magnetic field lines parallel to the plasma axis. In this case, the electron drift-diffusion perpendicular to the magnetic field is impeded but increases with collisions and large Larmor radius while in the direction parallel to B, the transport is unmodified. To simplify data analyses, LP measurements have been performed from z = 2 cm, position shown by a vertical dashed line in Fig. 3 where B has already strongly decreased. Approximations made to analyze LP characteristics up to z = 9 cm will be specified in the text.

B. Langmuir probe measurements

A complete modelling of I-V cylindrical probe characteristics can be found in the literature when drifting Maxwellian electrons are considered in magnetron discharges.[42] As shown, if one considers only axial magnetic fields, perpendicular drift velocities of plasma particles are ignored. In the parallel direction of B, electron drift velocities can be large and the amount of electron current collected at a given probe bias increases with v_d/v_{th} where v_d (v_{th}) is the electron drift (thermal) velocity. Conversely, when $v_d/v_{th} \leq 0.32$ the classical LP treatment can be used. Moreover, it was shown that when a cylindrical probe is moved perpendicularly to the magnetic field lines, the magnetic field influence on the probe charge collection becomes negligible if the ratio $r_p/r_L \leq 1$, r_p and r_L being the probe radius and electron Larmor radius, respectively.[43-

[45] In the presented experiments, both conditions were verified subsequently for $z \geq 2$ cm. Therefore, the conventional LP model was used.[46]

Measurements made it possible to check the cylindrical symmetry of the discharge at least from r = -2 to 2 cm.[37] For this reason in Fig. 4 (a)-(d), plasma parameters are only shown from r = 0 cm to the glass tube position at r = 6 cm, in the (r, z) plane. The cathode and the guard ring are schematized at the top of each figure and the magnetic field lines deduced from measurements are superimposed on some of them. They consist of magnetic arches until the magnetic null point at z ~ 3.4 cm and by almost perpendicular lines to the anode plate. Figure 4(a) shows that the maximum of electron density $n_e \sim 1.5\ 10^{17}\ m^{-3}$ is achieved inside the magnetic arch at z = 2 cm. From z ~ 3.4 cm, the maximum is obtained on the discharge axis. From this position, an axial decrease is observed going towards the anode plate and going towards the plasma edge with a minimum of $\sim 5\ 10^{14}\ m^{-3}$ at z = 9 cm. These results are consistent with models and other LP measurements showing that the maximum of plasma density is reached above the cathode racetrack.[47-49]

Figure 4(b) shows variations of the electron temperature T_e. Magnetic field lines were not superimposed for more clarity. Inside magnetic arches, T_e is lower than all around and the minimum is found where n_e is maximum. A second minimum appears at r = 4-5 cm under the guard ring. The maximum of 1.8 eV is reached at the plasma edge. These results illustrate the general trend of plasmas where to sustain the discharge, T_e increases when n_e decreases. From the null point towards the anode plate, T_e decreases as n_e. The lowest value of ~ 0. 75 eV is found at z = 9 cm.

The cooling of T_e in presence of metal sputtered atoms of low ionization potential has already been reported.[50] W ionization potential is 7.86 eV against 15.76 eV for Ar. Hence, we assume that W ionization takes place when $z < 2$ cm since no W^+ line was observed for $z \geq 2$ cm by optical emission spectroscopy aiming parallel to the cathode (not shown here). This assumption is consistent with modelling showing that at fairly high pressure, the ionization develops near the racetrack and closer than at low pressure.[47,51,52] For $z > 6$ cm, T_e is smaller than 1 eV, this indicating that Ar ionization-excitation is reduced to negligible levels. Only W atomic lines were observed in this region until z = 8 cm where the plasma emission was extremely low.

Figure 4(c) shows that the plasma potential is negative inside the magnetic arche ($V_p \sim$ -0.2 V) at z = 2 cm. A steep increase is observed going towards the last magnetic arch. The maximum of positive values is reached under the guard ring (~ 1.3 V). From z = 4 cm, V_p

decreases slowly to z = 9 cm and to the plasma edge. These measurements indicate that the cathode presheath extends up to 2 cm where V_p is still negative. This result is consistent with other measurements and with models showing that at low pressure, the presheath can have several centimeter widths.[53] At very low gas pressure, it was also shown that when V_p becomes positive, it progressively increases or saturates in the background plasma[54] while in MS-GAS for instance, used at higher pressure for the production of NPs of Ti,[48] a decrease of V_p was found as in our experiments.

C. Laser induced fluorescence measurements

Variations of the gas temperature were studied through Ar atoms in the $1s^5$ metastable state. The latter undergo the optical transition $1s^5 \rightarrow 2p^7$ corresponding to the laser wavelength, $\lambda_0 =$ 772.38 nm. The fluorescence emission from the excited state $2p^7$ towards the lower level $1s^4$ is 810.4 nm. Due to the Doppler shift, the laser frequency is resonant with the incident transition only if the atom velocity $v = c(\upsilon_l - \upsilon_0)/\upsilon_l$ where υ_0 is the transition frequency of an atom at rest, υ_l the laser frequency and c is the speed of light in vacuum. Doppler shift is related to the temperature T of the metastable argon atom population by:

$$k_b T = \frac{\lambda_0^2\, M}{8\ln 2}\Delta\nu^2 \qquad (1)$$

where k_b is the Boltzmann constant, $\Delta\nu$ is the full width at half maximum of Doppler shift and M the atom mass. With a vertical polarization E_0 of the beam at the entrance of the plasma and according to the selection rules of $2p^7$ level, three π Zeeman transitions should be considered when $E_0 // B$ and six σ Zeeman transitions when $E_0 \perp B$. Figure 5 (a) shows in black the average of three successive LIF signals obtained at 90° of the incident laser beam at (r, z) = (0 cm, 1 cm) where $B_{//} \sim 470$ G and $B_\perp \sim 7$ G (laser beam at grazing angle of the guard ring). The best Gaussian fit in black gives a temperature of 3256 K. Considering a negligible contribution of σ transitions, the three corresponding π transitions are represented in colour and give a temperature of 3263 K. Temperatures being similar, effects of π Zeeman transitions were neglected for r $\geq$ 2 cm where Langmuir probe measurements were made. The same procedure was followed at z = 1 cm and r ~ 2.2 cm, position of the maximum of a magnetic arch. Six σ transitions were calculated considering only a perpendicular magnetic induction to E_0 ($B_\perp \sim$ 230 G and $B_{//} \sim 5$ G). They are represented in color Fig. 5(b). The best Gaussian fit of experimental signals gives 2003 K and σ Zeeman transitions give 2135 K (~ 7% larger). However, the almost exponential decrease of B when z increases and due to the fact that temperatures are quite high, σ Zeeman transitions give temperatures similar to that of the best Gaussian fits of LIF signals for z ≥ 2 cm and do not exist beyond the null point. Therefore, these transitions were also neglected.

Figure 4(d) shows the mapping of gas temperature T_{ar}, assuming the thermal equilibrium between metastable argon atoms and all other argon atoms in the discharge. Measurements at z = 5 cm were extended linearly up to 300 K the temperature of the anode plate, this giving a temperature around 400 K at z = 9 cm. In the part where LP measurements were performed, the highest temperature was obtained on the discharge axis (~ 1465 K). From this position, axial and radial decrease were measured except at r ~ 2.2 cm for z = 3-4 cm where a slight increase was also measured.

At relatively high pressure and assuming the cathode at room temperature thanks to water cooling, the gas heating is mainly due to collisions with sputtered atoms of high mean energy. When these atoms are W, it was shown that their energy distribution function (EDF) established with Thompson model[55] is consistent with the EDF found with molecular dynamic simulations by taking incident energies of 150 - 200 eV for Ar^+.[56] In this energy range close to our conditions, the EDF maximum of sputtered atoms at the cathode surface given by Thompson model is around half of W binding energy (E_b = 8.9 eV) and their mean energy is near 12 eV. Large gas temperatures in the cathode region were already reported for other metals such as Fe[57] or Cu against Al cathodes using the LIF diagnostic.[58] Moreover, three-dimensional simulations have shown that the maximum of gas temperature in magnetron discharges is obtained on the axis and the position of the heated volume comes closer to the target when the pressure increases.[58]

III. NANOPARTICLE CHARGE AND APPLIED FORCES

A. Nanoparticle charge with the OML model approximation

Plasma parameters presented in the previous chapter are inhomogeneous and are typical of magnetron discharges. Therefore, they are expected to generate inhomogeneous NP charges and applied forces whether electrical or thermal. Conversely, we will assume that NP effects on the discharge parameters are weak and will only consider in a first approach, the charging mechanism and transport of a single NP.

When $a \ll r_L$ where a is the NP radius, magnetic field effects on the dust charge are insignificant.[45] Moreover, the conditions of the OML model in a collisionless plasma for the determination of the collected current by an isolated particle assumes that $a/\lambda_D \ll 1$ where λ_D is the linearized Debye length approximately equal to the ion Debye length, λ_{Di} (2 μm < λ_{Di} < 50 μm). If ions are governed by a Maxwellian distribution, the ion flux to a negatively charged particle is:

$$J_i(\phi) = J_{i0}\left(1 - \frac{e\phi}{k_B T_i}\right) \quad (2)$$

where ϕ is the negative NP floating potential with respect to V_p. $J_{i0} = 1/4 e n_0 v_i$ is the random ion current density where n_0 is the plasma density assuming electron and ion neutrality. T_i and $v_i = (8k_BT_i/\pi M)^{1/2}$ are the ion temperature and thermal velocity, respectively. For a weak electric field in the plasma, the ion temperature can be approximated by $T_i \sim T_{ar}$.[59] This requires verifying the criteria $E/N < 20$ Td where E is the electric field, N the gas density at the considered temperature and where E/N is expressed in Townsend (1 Td = 10^{-21} Vm^2). Hence, the axial and radial components of the electric field (E_z and E_r, respectively) have been calculated according to $\vec{E} = -\vec{\nabla} V_p$. For this, V_p measurements every centimeter were interpolated with a step of 0.05 cm. Figure 6(a) shows the resulting mapping of E (V/m). Even if local variations of E inform about the limited spatial resolution of V_p, they may reveal the existence of two regions: i) inside magnetic arches E increases as z, ii) E is nearly constant outside. Both regions are separated by a sharp transition near the last magnetic arch corresponding to V_p inflexion points. The maximum is around 110 V/m and outside the transition, the electric field is around 15 V/m. Consequently, in the region defined by i) we have found: $2 < E/N$ (Td) < 16 for $z \leq 4$ cm where N has been deduced from P_{ar}/T_{ar} and in the region defined by ii) E/N (Td) < 2. Hence, both conditions have allowed taking $T_i \sim T_{ar}$. In addition, in presence of a weak E field, one can consider the ion drift velocity $u_{di} = \mu_i E$ where $\mu_I = e/M\nu_{in}$ is the ion mobility and $\nu_{in} = N\sigma v_i$ is the momentum transfer frequency in ion-atom collisions. The cross section σ can be evaluated considering that the energy gained with E is lost through elastic scattering and charge-exchange collisions with argon atoms. The cross section of charge transfer $\sigma_{CX} = 6.82\ 10^{-19}$ m^2 and elastic scattering $\sigma_m = 1.57\ 10^{-18}$ m^2 were deduced from Phelps data[60] for an ion energy corresponding to a temperature of 1000 K. Figure

6(b) shows that the mapping of u_{di} in (m/s) reproduces the complex electric field variations. The maximum is around 110 m/s in the transition region of E while drift velocities are negligible in the background plasma where $u_{di} < 20$ m/s and where the thermal velocity is $v_i \sim 730$ m/s at the considered temperature. However, in the case of a sub-thermal flow and taking an ion distribution approximated by a shifted Maxwellian function, the ion flux to the dust particle is given by:[61-63]

$$J_i(\phi) = J_{i0} \left[\frac{\sqrt{\pi}}{4u}\left(1 + 2u^2 - 2\frac{e\phi}{k_B T_i}\right) \mathrm{erf}(u) + \frac{1}{2}\exp\left(-u^2\right) \right] \qquad (3)$$

where u is the ion drift velocity normalized to the ion thermal velocity.

As for LP data analyses, it will be assumed that electron drifts are negligible and if electrons are governed by a Maxwell-Boltzmann distribution, the electron flux to the NP is given by:

$$J_e(\phi) = J_{e0} \exp\left(\frac{e\phi}{k_B T_e}\right) \qquad (4)$$

where $J_{e0} = -1/4 e n_0 v_e$ is the random electron current density, $v_e = (8k_B T_e/\pi m_e)^{1/2}$ is the electron thermal velocity and m_e the electron mass. In the OML approach, the equality between (2) and (4) gives the charge carried by a NP: $Q = 4\pi\varepsilon_0 a\emptyset = -eZ$, where e is the elementary charge. Taking $a = 5$ nm the characteristic radius of NPs on the guard ring surface and considering spatial variations $T_i \sim T_{ar}$, Fig. 7 shows the contour plot of Z. The ion thermal velocity being smaller than the electron one, the maximum $Z \sim 18$ is found in the upper midplane where T_e is maximum i.e. at the limit of the last magnetic arch and at the plasma edge. For $z > 4$ cm, Z decreases progressively towards the anode plate. As expected, the equality between (3) and (4) gives NP charges that differ only by 0.5% in the better case of charges found equating (2) and (4).

B. Applied forces

The transport of a dust particle in a plasma is due to various forces. In presented conditions, the main ones are the electric force F_e and the ion drag force F_i, which both depend on Q and the thermophoretic force F_{th} due to fairly large gas temperature gradients. It will be shown that the gravity and the gas drag forces are negligible. The electric force exerted on a dust particle due to plasma potential variations is:

$$F_e = QE \quad (5)$$

Figure 8(a) shows the 2D mapping of F_e in 10^{-16} N. The superimposition of the magnetic field lines shows as expected, the region of maxima in the limit of the last magnetic arch (maximum of 2.7 10^{-16} N). Figure 8(b) shows the direction of vectors and reveals that F_e pushes the negatively charged NP out of magnetic arches. For r ≥ 3 cm and in the upper midplane of the plasma (z ≤ 4 cm), forces around 10^{-16} N push the particle towards the grounded guard ring. In the lower midplane, smaller forces in the range of 10^{-17} N are generally directed upward. At the edge of the plasma (r = 6 cm) all along z, the NP is pushed towards the core of the plasma as for electrons in the positive sheath of a plasma device.

The ion drag force F_i is associated to momentum transfer due to relative ion drift. It presents two contributions: a collection force and a scattering force. The general expression is: [22]

$$F_i = m \int \mathbb{v} \mathrm{v} f_i(\mathbb{v})[\sigma_c(\mathrm{v}) + \sigma_s(\mathrm{v})]\, d^3\mathbb{v} \quad (6)$$

where $f_i(\mathbb{v})$ is the ion velocity distribution function, and $\sigma_c(\mathrm{v})$ and $\sigma_s(\mathrm{v})$ are the momentum transfer cross sections for ion collection and scattering, respectively. As used to establish Eq. (2), the conservation of angular momentum and energy (OML model) gives: $\sigma_c(\mathrm{v}) = \pi\rho_c^2 = \pi a^2(1 + 2e\emptyset/(m\mathrm{v}_i^2)$ where ρ_c is the maximum impact parameter at which ions are collected. The Coulomb scattering cross section for ions approaching the dust is given by: $\sigma_s(\mathrm{v}) = 4\pi\int_{\rho_{min}}^{\rho_{max}} \rho d\rho/(1 + (\rho/\rho_0)^2 = 4\pi\rho_0^2\Gamma$, where Γ is the Coulomb logarithm and $\rho_0 = Ze^2/(4\pi\varepsilon_0 m\mathrm{v}_i^2)$ is the Coulomb radius. $\rho_{min} = \rho_c$ and since the parameter $\beta = \rho_0(\mathrm{v})/\lambda_D << 1$, it can be considered that beyond λ_D, ions do not feel the particle. Therefore, $\rho_{max} = \lambda_D$ (standard Coulomb scattering) and Coulomb logarithm reduces to $\Gamma = 1/2\mathrm{Ln}(1+1/\beta^2)$.[21,25] Moreover, when $u_{di}/\mathrm{v}_i << 1$, a simplified shifted Maxwellian distribution function was proposed to establish the ion drag force:[25] $f_i(\mathbb{v}) \sim f_0(\mathbb{v})(1 + u_{di}\mathbb{v}/\mathrm{v}_{Ti}^2)$ where $f_0(\mathbb{v})$ is the isotropic Maxwellian distribution. The integration of Eq. (6) with the approach of the standard Coulomb scattering gives:[25]

$$F_i = \frac{4}{3}\pi a^2 n_0 \mathrm{m}\, \mathrm{v_i} u_{di}(1 + \frac{\rho_0}{2a} + \frac{\rho_0^2}{4a^2}\Gamma) \quad (7)$$

The first two terms in parenthesis represent the contribution of the collection part, which is negligible compared to the contribution of Coulomb scattering given by the third term. Figure 8(c) shows the mapping of F_i which varies exactly inversely to F_e. As for F_e, there is a clear boundary near the last magnetic arch. Inside this limit, F_i is larger than outside. The maximum of ~ 1.1 10^{-16}N is reached at (r, z) = (3 cm, 2 cm). In the lower midplane values are in the range of 10^{-17}- 10^{-18} N, indicating that F_e dominates F_i everywhere when a = 5 nm.

The presence of substantial gas temperature gradients is at the origin of another force known as the thermophoretic force. Gas atoms in hotter areas have larger velocities and transfer more momentum to the NP than in cooler areas. This causes a net force in the direction of $-\nabla T_{Ar}$. In the following, it will be considered that the gas is only composed of argon atoms. For a << L_N where L_N is the atom collision mean free path, the gas is in a molecular regime and a simplified expression of the thermophoretic force in this situation is given by:[64]

$$F_{th} = -\frac{32}{15}\frac{a^2}{\mathrm{v_{th}}} K_{th}\,\nabla T_{Ar} \qquad (8)$$

where $\mathrm{v_{th}}$ and K_{th} are the argon thermal velocity and conductivity, respectively. K_{th} varies with the temperature as $K_{th} = \sum[\mathrm{C(N)T^N}]$. Coefficients C(N) are known from N = 1 to N = 6 for the temperature range 300 K ≤ T ≤ 1000 K and give thermal conductivities varying from 17.67 10^{-3} $Wm^{-1}K^{-1}$ to 42.71 10^{-3} $Wm^{-1}K^{-1}$. [65] Fig. 8(d) shows that the maximum of F_{th} (~ 2.1 10^{-16} N) is on the plasma axis at z = 2 cm. From this position, F_{th} pushes the particle towards the bottom and plasma edge (cold regions). At z = 3 cm, there is an inversion of F_{th} due to a slight increase of T_{ar} measured along the corresponding line of sight. In the lower midplane, F_{th} is slightly larger on average than F_e and is therefore dominant.

Other forces can act on dust particles but are here negligible compared to those already presented. There is the neutral drag force F_N where neutral particles transfer their momentum to the dust particle. When a << L_N, the expression of F_N in the molecular regime is given by: [22,28]

$$F_N \sim 8\sqrt{2\pi}/3\; a^2 N M \mathrm{v}_{th} u_n \qquad (9)$$

where u_n ~ 0.4 cm/s is the velocity of Ar atoms in the low gas flow of 5 sccm. When a = 5 nm, F_N ~ 5 10^{-20} N is three to four orders of magnitude smaller than F_e.

The gravitation force can also be considered. It is given by the simple expression:

$$F_g = 4/3\pi a^3 \rho_W g \qquad (10)$$

where ρ_W is the tungsten mass density and g the gravitational acceleration. When a = 5 nm, F_g~ 9 10^{-20} N and is also three to four orders of magnitude smaller than F_e.

IV. BALANCE OF APPLIED FORCES

Figure 9(a) shows the balance of applied forces for a = 5 nm, the average radius measured on the guard ring after 10 plasmas of 200 s. Only F_e and F_{th} have an influence. In the upper midplane, F_e is the greatest force: when the NP is under the guard ring, it is pushed with F_e to this area. When the NP is near the plasma axis, F_e as well as F_{th} push it out of magnetic arches and towards the substrate located at 10 cm from the cathode. F_{th} is the dominant force whatever the position in the lower midplane and push down the particle. The strength of this force increases when the NP radius increases ($\propto a^2$) compared to the electric force ($\propto a$), and for the same plasma duration, measurements on substrate have shown that a = 15 nm on average. Figure 9(b) gives the norm and the direction mainly towards the anode plate of the resulting forces applied to a NP of a = 15 nm radius. It is essentially dominated by F_{th} in the lower midplane. This result means that a NP which is pushed down from z = 2 cm to z = 10 cm can have enough space and time to grow by accretion[12] up to a = 15 nm meanwhile the particle which is pushed towards the guard ring (nearest position of W source) can only grow to smaller sizes (a = 5 nm) before deposition. Let us notice that F_i ($\propto a^2$) is around one order of magnitude smaller than F_{th} when a = 15 nm. Therefore, F_i has no influence on the dust transport in these conditions. More generally, this basic modelling of the force balance in 2D dimensions shows that when sputtered metal atoms (W, Ti, Cu, Al …) of mean energy ~ 10 eV are thermalized with the buffer gas, it is finally the thermophoretic force that pushes the NP towards the anode plate where the collection is usually made.

V. CONCLUSION

The charge and forces applied to an isolate NP in conventional magnetron discharges were established using basic models. In the field of NP production where the control of sizes is a sensitive issue, the goal was to explain why for a given plasma, different sizes were found depending on the position of deposits. First, 2D measurements of plasma parameters were performed and correlations with the magnetic field lines and strengths were established. The plasma parameters have allowed to calculate 2D variations of the negative charge of the particle as well as the electric and ion drag forces applied to it. The thermophoretic force due to large gas temperature gradients induced by the sputtered atom thermalization was also established. The force balance was studied for the average size measured on the grounded guard ring i.e. the anode located around the cathode. We have shown that only electric and thermophoretic forces have an influence. When the particle is near the guard ring, it is mainly pushed by the electric force towards the guard ring. In the lower midplane of the plasma, the thermophoretic force is always dominant and pushes the particle towards the coldest regions, in particular towards the anode plate parallel to the cathode. Therefore, in the plasma region separating both electrodes, the NP can have enough space and time to grow by accretion, this reinforcing the role of the thermophoretic force proportional to the square radius. In magnetron discharges, this can explain why the average size in NP deposits near the anode plate where the samples are usually taken is larger than on the guard ring located around the sputtering source.

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FIGURE CAPTIONS:

FIG. 1. Experimental set up (color online). Upper part: scheme of the magnetron setup; lower part: top view of diagnostics.

FIG. 2. Nanoparticles produced by 10 successive plasmas of 200 s (a) collected on a substrate at 10 cm of the cathode, (b) collected on the grounded guard ring located around the cathode. (c) Guard ring with a thin layer of nanoparticles on the surface.

FIG. 3. Magnetic field strength as a function of position z for r = 0 cm (cathode center), r ~ 2.2 cm (average position of the cathode racetrack) and r = 5 cm (under the guard ring), the magnetic null point being at z = 3.4 cm on the discharge axis. Langmuir probe measurements performed from z = 2 cm are shown with a vertical dashed blue line.

FIG.4. 2D mappings of plasma parameters measurements: (a) electron density n_e, (b) electron temperature T_e, (c) plasma potential V_p and (d) argon temperature T_{ar}. Magnetic field lines superimposed in (a) and (c).

FIG. 5. Laser beam at grazing angle of the guard ring (z = 1cm). (a) In black, average LIF signal recorded at 90° from the incident laser direction at r = 0 cm where E_0 // B and fitted by a Gaussian function. The three corresponding π Zeeman components are in colour. (b) In black, average LIF signal recorded at r = 2.2 cm where $E_0 \perp B$ and fitted by a Gaussian function. The six corresponding σ Zeeman components are in colour.

FIG. 6. (a) 2D mapping of the plasma electric field. (b) 2D mapping of the ion drift velocity.

FIG. 7. Charge Z of a nanoparticle of radius a = 5 nm given in elementary charges.

FIG. 8. (a) 2D mapping of the electric force F_e applied to an isolated nanoparticle with superimposition of magnetic field lines; (b) F_e with superimposition of vectors. (c) 2D mapping of the ion drag force F_i. (d) 2D mapping of the thermophoretic force F_{th}.

FIG. 9. Balance of forces applied to a nanoparticle (a) of radius a = 5 nm measured on the guard ring, (b) of radius a = 15 nm measured on a substrate located at 10 cm of the cathode, for the same plasma duration.