Nucleation and growth of magnetron-sputtered Ag nanoparticles as witnessed by time-resolved small angle X-ray scattering

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Abstract

Kinetic aspects of the synthesis of Ag nanoparticles (NPs) by magnetron sputtering are studied by *in situ* and time-resolved Small Angle X-ray Scattering (SAXS). Part of the NPs are found to become confined within a capture zone at 1 – 10 mm from the surface of the target and circumscribed by the plasma ring. Three regimes of the NP growth are identified: 1) early growth at which the average NP diameter rapidly increases to 90 nm; 2) cycling instabilities at which the SAXS signal periodically fluctuates either due to expelling of large NPs from the capture zone or due to the axial rotation of the NP cloud; 3) steady-state synthesis at which stable synthesis of the NPs is achieved. The NP confinement within the capture zone is driven by the balance of forces, the electrostatic force being dominating. On reaching the critical size, large NPs acquire an excessive charge and become expelled from the capture zone *via* the electrostatic interactions. As

a result, significant NP deposits are formed on the inner walls of the aggregation chamber as well as in the central area of the target.

1. Introduction

Synthesis of metal nanoparticles (NPs) by magnetron sputtering with subsequent condensation in a cold buffer gas has been attracting strong scientific interest for years.¹ This approach benefits from the vapourization of metals *via* the bombardment by energetic ions, rather than by purely thermal means, which allows virtually any metal to be sputtered and its atomic vapours to be supplied into the gas phase. Sputtered atoms escape from the target with hyperthermal energy and are forced to thermalize upon the interaction with the atoms of the cold inert gas, resulting in the spontaneous nucleation and formation of NPs. The inert gas flow is typically created to drag the NPs from the aggregation zone into another vacuum chamber where they can be collected on substrates.

The employment of highly non-equilibrium conditions favors tailoring the morphology of resultant NPs which strongly depends on the rate with which NPs equilibrate themselves with the ambient gas.²⁻⁵ Furthermore, mixing of two or more metals can be realized either simultaneously or sequentially giving rise to a wealth of homogeneous or heterogeneous nanoalloys, unattainable by conventional means.⁶⁻¹⁸ Despite great progress in laboratory synthesis of novel NPs with advanced functionalities, commercial applications of magnetron-sputtered NPs are still far from being at hand. A major obstacle for the commercialization is commonly seen in the uncompetitively low rate of the NP deposition on surfaces which is related to a generally recognized issue of the loss of the NPs inside the aggregation chamber before they leave it. Solving this problem is still quite challenging because of the knowledge gap that exists between the understanding of the atomistic processes of sputtering and the processes of the NP formation, growth and transport under the conditions of the magnetron discharge.

In our previous works, the new findings on the mechanisms of the gas phase formation of Cu NPs were revealed by *in situ* Small Angle X-ray Scattering (SAXS) analysis¹⁹ and UV-Vis spectroscopy.²⁰ As was shown, Cu NPs are formed at a very short distance from the magnetron target; moreover, their average size and the relative volume fraction demonstrate strong non-linear distribution along the aggregation zone. This effect was the most pronounced at a distance

of 1 – 10 mm from the target where untypically large Cu NPs with the average diameter of 80 nm were detected.

The present work investigates the synthesis of Ag NPs with the purpose to highlight the common features between the two metals. We utilize the similar SAXS diagnostics, yet at a more sophisticated level. *In situ* SAXS measurements are employed in a time-resolved mode to unveil the kinetic aspects of the Ag NP formation, growth and transport, and to address the issue of the NP loss within the aggregation chamber.

2. *Experimental*

A custom gas aggregation cluster source (GAS) was built to ensure arbitrary X-ray probing positions within the inner volume of the aggregation chamber (Scheme 1, for the experimental details see Supporting information). The GAS consisted of a 100 mm diameter stainless steel chamber cooled by water and terminated by a conical lid with an exit orifice of 2.0 mm in diameter. A moveable 3-inch magnetron with a 3 mm thick silver target (Safina, A. C. 99.99% purity) was installed in the GAS. The magnetron was run by a DC power supply (Advanced Energy MDX500) operated in a constant current regime with the current set to 600 mA and the corresponding voltage of 313 V. A toroidal-shaped plasma ring with a diameter of 40 mm was maintained by a circuit of permanent neodymium magnets installed inside the magnetron. A pair of transversal 100 mm viewports with 125- μ m thick KaptonTM windows provided an access for the X-ray beam to the interior of the GAS.

The GAS was mounted onto a main deposition chamber evacuated by scroll and turbomolecular pumps to a base pressure of 10^{-4} Pa. Quartz Crystal Microbalance (QCM) was positioned inside the deposition chamber in front of the exit orifice to monitor the deposition rate of the NPs measured in terms of the QCM frequency shift. Argon was used as a buffer gas at a pressure of 133 Pa and a flow rate of 18 sccm. The entire assembly was installed at the P03 beamline of PETRA III, DESY, Hamburg, Germany.²¹ An electrically actuated mobile platform was used to allow for the axial positioning of the entire experimental setup with respect to an X-ray beam (photon energy is 13.01 keV, elliptically microfocused to $22 \times 32 \mu\text{m}$, $V \times H$ axes). SAXS measurements with variable x were performed, where x is the axial distance from the magnetron target. In this configuration, the X-ray beam passes above the target and crosses its

entire diameter so that the probed space involves two regions of the plasma ring and the central region. Time-resolved measurements were performed with a frequency of 10 Hz, with 95 ms acquisition time followed by 5 ms read-out time per image using a Pilatus 300 K detector (Dectris Ltd., pixel size 172 μm) in a distance of (5642 ± 8) mm to the centre of the GAS. The data were processed using the software DPDAK,²² a customizable code for the analysis of large SAXS data, as described in the Supporting information.

Scanning Electron Microscopy measurements of the target were performed using a microscope Supra55VP-Carl Zeiss equipped with an in-lens detector. The acceleration voltage was 5 kV. Series of the experiments were performed with silicon substrates (<100> Si, one-side polished, 525 ± 15 μm thick, ON Semiconductor, Czech Republic) positioned inside the aggregation zone at different distances from the target. These samples were analysed by a Tescan Mira III SEM microscope equipped with an in-beam SE detector with acceleration voltage of 20 kV.

The profilometry measurements were performed with a Bruker DektakXT profilometer. The applied force on the stylus was 1mg and the obtained resolution was 0.46 μm .

A fluid flow analysis inside the aggregation chamber was performed using a Computational Fluid Dynamics (CFD) software (Siemens STAR CCM+ 13.04.010). The analysis was done in a steady-state mode employing a segregated flow solver with 2nd order convection. A Semi-Implicit Method for Pressure Linked Equations (SIMPLE) pressure-velocity coupling algorithm was used. The boundary conditions were set to be: the system pressure is 133 Pa, the inlet gas flow is 18 sccm, the Ar temperature is 20 °C. For more detail, see Supporting information.

Scheme 1 Experimental setup. The gas aggregation cluster source is moveable with respect to the X-ray beam along the x -axis which allows for probing Ag NPs at different axial distances from the magnetron target, acquiring SAXS signal at the detector, reconstructing the scattering intensity as a function of the magnitude of the wave vector q and fitting these curves to obtain the NP size distribution and relative volume fraction.

3. Results

Time-averaged SAXS curves were processed to obtain the axial dependence of the average diameter d of Ag NPs and their relative volume fraction f_{rel} (the parameter directly proportional to the ratio of the volume occupied by all the NPs to the sampled volume defined by the beam size) which are shown in Fig. 1 along with the earlier reported data for Cu NPs. Similar trends were confirmed: both parameters grow fast in the close proximity to the magnetron target, reach maximal values and then decay to constant levels at farther distances. Designated earlier as the capture zone, the range of $x = 2 - 5$ mm is characterized by the presence of large NPs with the average size reaching 80 nm. Nevertheless, the NPs of this size were found only sporadically on the substrates placed outside the GAS.

Fig. 1 a) average diameter; b) relative volume fraction of Ag and Cu NPs (data used from ref.¹⁹) in dependence on the axial distance in the GAS with the radial distance fixed at $y = 0.0$ mm. The position $x = 0.0$ mm corresponds to the surface of the target. The vertical dotted line shows the position of the exit orifice of the GAS at $x = 120.0$ mm. Error bars are standard deviation obtained from fitting of 90 individual scattering curves at each spatial position.

Fig. 2 Evolution of: a) the average diameter d ; b) the relative volume fraction f_{rel} of Ag NPs produced in the GAS at $x = 2.2$ mm; c) the deposition rate (in terms of QCM frequency shift) outside the GAS at $x = 200.0$ mm. The values of time $t = 0$ and 60 s correspond to turning the discharge on and off. The second population of the NPs (open symbols) was added to the fit of the scattering curves whenever the monomodal size distribution was not sufficient to fit the data correctly (for details see Supporting information). Three periods of the NP formation in the GAS are identified: 1) nucleation and early growth; 2) cycling instabilities; 3) steady-state synthesis.

Time-resolved SAXS measurements were performed to obtain the kinetic information about the NPs in the vicinity of the magnetron target. The discharge was turned on for 60 s and the SAXS data were acquired with a time step of 100 ms. Fig. 2a, b show the time dependence of the

average NP diameter and the relative volume fraction obtained in this manner for the position $x = 2.2$ mm where the scattering intensity was maximum. For reference, Fig. 2c shows the time dependence of the deposition rate of the NPs measured outside the GAS at $x = 200.0$ mm in terms of the QCM frequency shift. Three periods can be identified.

1) In the early regime (0 – 2 s), both the NP diameter and the relative volume fraction rapidly increase, yet QCM does not detect any deposition rate.

2) In the second regime (2 – 16 s), significant fluctuations of the scattering signal are observed, although none are present in the QCM signal which starts increasing after an initial lag. The scattering curves periodically deviate from the shape characteristic for the monomodal NP size distribution. At these phases, bimodal size distribution is introduced to fit the data and two sets of the average size and the relative volume fraction are shown for two populations of the NPs (for more detail, see Supporting information).

3) In the third regime (16 – 60 s), the fluctuations subside and a steady-state generation of the NPs is reached which is accompanied by a constant deposition rate. It is worth noting that the SAXS signal disappears very fast after turning off the discharge at $t = 60$ s, although QCM demonstrates a lag of the same duration as in the beginning. The lag is finished by an abrupt burst of the deposition rate followed by its decrease to zero.

Peculiarities of the three regimes are scrutinized separately in the subsequent sections.

3.1. Early growth

The time dependencies of the average NP diameter and the relative volume fraction were calculated for 12 axial positions in the vicinity of the magnetron target. Fig. 3 shows selected data for clarity. The NP diameter increases almost linearly with time for the entire set of x . The relative volume fraction also increases close to the linear time dependence. This parameter is directly proportional to the total volume occupied by all NPs within the sampling volume and hence is proportional to the molar concentration of Ag atoms bound within the NPs $[Ag_{NP}]$. If a simplistic condensation scheme is considered in which Ag atoms pass from the vapour to the bound state $[Ag_{vapour}] \rightarrow [Ag_{NP}]$, the linear character of the function $[Ag_{NP}] = kt$ points to the realization of this scheme via a zero-order scenario: the reaction rate does not apparently depend on the concentrations of reactants and is equal to the reaction constant k . In our case, this means

that the concentration of atomic Ag vapour state remains to be in large excess and that it cannot be a limiting factor for the formation of Ag NPs for the entire set of x .

The rate of the condensation $d[\text{Ag}_{\text{NP}}]/dt$ shows a complex dependence on the axial position (Fig. 3). At small x , it increases with the axial distance and reaches the maximum for $x = 2.2$ mm. At farther distances from the magnetron target, the rate starts decaying and drops to very low values at $x = 10.7$ mm. Such complex behavior will be analyzed later in the *Discussion* section. Here, we stress that f_{rel} retains close-to-linear time dependence for all x and therefore the concentration of atomic Ag vapours remains sufficiently high not to limit the NP formation and growth. This conclusion also agrees with a concept of super-saturation which is required to induce spontaneous nucleation of NPs and which implies that super-saturated (high) metal vapour pressure is continually replenished. Thus, the nucleation of Ag NPs occurs in the entire axial range in question.

Fig. 3 Time dependence of a) the average Ag NP diameter d and b) the relative volume fraction f_{rel} measured at different axial positions. Time $t = 0$ corresponds to the ignition of the discharge. The dotted line shows the example of the linear extrapolation of the data to the NP diameter $d = 0$ nm, the time point taken as the moment at which the smallest NPs are born (the NP appearance time).

Low concentration of the NPs in the gas phase does not allow for the reliable processing of the scattering curves in the high- q region, and the detection of the NPs with the average size < 20 nm is impeded at the present experimental configuration. This shortcoming explains the fact that the NP size dependencies start with the values of about 20 nm and do not show smaller NPs. The extrapolation of the $d \sim f(t)$ data can be performed to the point of $d = 0$ nm and thus-obtained values of t can be used to estimate the moment at which the first nuclei are formed after the ignition of the discharge (we will designate this moment as the NP appearance time, t_a). Despite

seemingly overlapping, the curves in Fig. 3a provide different values of t_a , which align into a linear dependence if plotted as a function of the axial distance (Fig. 4). The linear fit to the data gives the value of 26 ± 3 mm/s which is consistent with the linear velocity of the gas flow in the GAS.

Fig. 4 Time at which NPs start to appear (the NP appearance time) at different axial distances from the magnetron target. The data are obtained by extrapolating the curves of Fig. 3a to the NP diameter $d = 0$ mm. The dotted line corresponds to the linear fit of the data.

Several important conclusions can be drawn at this point. The first NPs appear within a fraction of a second after the ignition of the discharge, the lag being larger at farther distances from the magnetron target. Once created, the NPs increase in size equally fast at different x and their growth is not limited by the partial pressure of atomic Ag vapours. These findings imply that nucleation is efficient in the entire range of axial positions studied (0 – 11 mm) and that the lag in the onset of the NP formation is given by the lag in the supply of atomic metal vapours from the target surface after the ignition of the discharge.

3.2 *Cycling instabilities*

After reaching the maximum size and concentration within approximately 2 s after turning on the discharge, NPs enter the regime of instabilities in which the NP parameters start to change in

an oscillating manner. The regime of cycling instabilities is analyzed in more detail in Fig. 5 where the average NP diameter d , the relative volume fraction f_{rel} and the relative number of NP N_{rel} (normalized to NP diameter) are shown for the axial position of maximal scattering intensity ($x = 2.2$ mm) in dependence on time at a zoomed time-scale. The relative number of NPs was calculated by dividing the relative volume fraction by the average NP volume ($N_{rel} = f_{rel} / (\frac{\pi}{6} d^3)$); it represents the quantity which is directly proportional to the concentration of the NPs within the volume sampled by the X-ray beam.

In the beginning of the cycle, the scattering curves are readily fitted by the monomodal lognormal size distribution (see Supporting information). The average NP diameter increases, the relative volume ratio remains constant and the number of NPs decreases. At a certain moment, the monomodal size distribution becomes insufficient to fit the data satisfactorily. The introduction of the second population of smaller NPs solves the problem (see also Supporting information). Hereafter, the first population of NPs proceeds in the growth but the volume they occupy and their number decrease. The NPs of the second population demonstrate the opposite behavior: they decrease in size but occupy the larger volume and increase in number. At the extremum, the average size of the first population reaches 85 nm whereas the average size of the second population decreases to 55 nm (here, we stress that these numbers are average values of lognormal size distributions with different values of dispersity). Then, the larger NPs disappear suddenly or, at least, they become undetectable by SAXS. Only smaller NPs are detected at this moment and the cycle is repeated. The scattering curves can be fitted with a monomodal size distribution again, the average NP diameter increases, the relative volume ratio remains constant and the number of NPs decreases until differentiation into other two populations of NPs occurs. The period of the described fluctuations is 1 s. For better visualization, an animation showing the evolution of the Ag NP size distribution was added to Supporting information. A more detailed reasoning about the interpretation of these oscillations follows in the Discussion section.

Fig. 5 Cycling fluctuations of: a) the average diameter d ; b) relative volume fraction f_{rel} and c) relative number N_{rel} of Ag NPs occurring in the GAS at $x = 2.2$ mm during the period of instabilities (period 2). The second population of the NPs (open symbols) was added to the fit of the scattering curves whenever the monomodal size distribution was not sufficient to fit the data correctly (for details see Supporting information). Serial numbers designate the N -th cycle ($N = 1, 2, 3 \dots$). The dotted line shows the sum of the relative volume ratios for the NP population 1 and 2.

3.3 Steady-state synthesis and extinction of the discharge

After the period of fluctuations, the generation of Ag NPs arrives to the steady-state regime at which the NP size and concentration do not change in time. An interesting phenomenon was observed when switching off the discharge: QCM detected stable deposition of NPs for a certain time followed by its sudden increase and then a decrease to zero (Fig. 1). A pulsing approach was applied to investigate this effect in more detail. The discharge was pulsed with time-on $t_{on} = 10$ s and time-off $t_{off} = 5$ s, and the deposition rate was monitored by QCM positioned outside the GAS at $x = 200.0$ mm (Fig. 6). It was confirmed that for each pulse no deposition occurs during

the first 3 s after turning the discharge on, then the deposition rate starts increasing and reaches the stable value at about 5 s, it remains stable at this level even after turning the discharge off at 10 s, then it sharply proliferates, but only for a short duration followed by a decrease to zero at 15 s, the time at which the next pulse is initiated. The time lag between the discharge turning on/off and the QCM response is readily explained by the time needed for NPs to travel along the GAS. When the distance of 120 mm between the magnetron target and the orifice is divided by the average linear gas velocity of 29 mm/s, the time of about 4 s is obtained that roughly matches the QCM lag (the 80 mm distance between the QCM and the orifice is neglected because NPs travel at much higher velocity in this region).

Fig. 6 The deposition rate of Ag NPs measured by QCM outside the GAS at $x = 200.0$ mm during pulsing the discharge with $t_{on} = 10$ s and $t_{off} = 5$ s: a) at longer time scale; b) the same dependence at shorter time scale.

The phenomenon of a manifold burst of the deposition rate with the discharge off can be analyzed by performing the time-resolved SAXS measurements in the pulsed discharge regime. Fig. 7 shows the changes observed in the average NP size, the relative volume fraction and the relative number of NPs after turning the discharge off at $t = 10.0$ s at different axial positions in the GAS. For the position of the highest scattering intensity at $x = 2.2$ mm, the NPs disappear within 0.2 s and the scattering intensity decreases to the background level. However at a farther distance of $x = 9.7$ mm, all the NP parameters show an increase for a fraction of second and then the intensity drops down as well. Markedly, the position closest to the magnetron target at $x = 0.2$ mm also demonstrates an interesting feature. The size of the NPs is too small for the detection at this position and the SAXS signal remains at the background level during the operation of the discharge. However, large 80 nm-sized NPs become detectable for a short period of 0.1 s after the discharge is turned off and then they also disappear. The short detection period explains the presence of only two data points for $x = 0.2$ mm in Fig. 7.

Fig. 7 Evolution of: a) the NP diameter d ; b) the relative volume fraction f_{rel} and c) the relative number N_{rel} after the discharge is turned off at $t = 10.0$ s for the position closest to the magnetron target ($x = 0.2$ mm), in the capture region with maximal scattering intensity ($x = 2.2$ mm) and

outside the capture region ($x = 9.7$ mm). Dotted lines are guide to eyes showing the decrease of the scattering intensity to the background level.

Thus, the following mechanism can be suggested. Part of the NPs becomes trapped in the capture zone when the discharge is on. The trapping results in a longer time that NPs spend in this region and, as a consequence, in an increase of their average diameter to the larger values. After turning the discharge off, the trapped NP cloud collapses and the large amount of NPs escape from the capture zone. After the time lag determined by the linear gas flow, the released multitude of NPs arrives to QCM and induces the short-time burst in the deposition rate.

Markedly, the NPs escape from the capture zone in the direction towards the magnetron target as well, that is against the gas flow (see the simulations of Ar velocity vectors in the Supporting information). Fig. 8 shows the photos of the target surface taken after 1 week of the experimental campaign. A macroscopic deposit of the NPs is formed in the central area of the target. The SEM images demonstrate that the deposit consists of coalesced NPs and a rough estimation shows that, although strongly coalesced, they have the average diameter of about 90 nm. This finding confirms that the NPs become trapped above the target in the region circumscribed by the magnetron plasma ring.

Fig. 8 Characterization of the target surface: a), b) top view and side view photos of the target showing the macroscopic re-deposit of Ag NPs in the central area (taken after 1 week of the experimental campaign); c) profilometry height profile of the re-deposit of NPs corresponding to

the dotted line on the top view image; d) and e) SEM images of the target surface acquired at the periphery (spot 1) and in the center (spot 2) after 10 s of sputtering of fresh target; f) size distribution of the NPs redeposited in the central area of target, the curve corresponds to the lognormal fit to the data, average NP diameter is $\mu = 89$ nm, standard deviation is $\sigma = 20$ nm.

Two sets of the experiments were performed with placing 0.5×0.5 cm Si substrates directly onto the inner wall of the aggregation chamber at different distance from the magnetron target. After installing the substrates, the GAS was evacuated, the experimental parameters were adjusted, the discharge was turned on for 10 s and then the sputtering was stopped. The substrates were extracted from the GAS and analyzed by SEM. The second set was performed in a similar manner, yet with the 60 s operation. The SEM analysis of the resultant deposits is shown in Fig. 9. Similar to the earlier notation, the position $x = 0$ mm corresponds here to the position of the target plane so that $x = -3$ mm corresponds to the substrate shifted by 3 mm behind the magnetron target.

Fig. 9 Top view SEM images of Ag NPs collected on Si substrates placed onto the GAS wall at different axial positions from the magnetron target: a) the deposition time $t = 10$ s; b) the deposition time $t = 60$ s.

Even after 10 s of sputtering, we observe the accumulation of NPs on the walls all along the aggregation chamber, the amount of the deposit being larger closer to the magnetron. Markedly, the NPs are effectively deposited even at the positions behind the target plane. The morphology of the deposits also changes. Closer to the magnetron at $x < 3$ mm, the deposit consists of spherical NPs arriving as-formed in the gas phase. A strong contribution from the large NPs can be seen here. At $3 < x < 39$ mm, irregularly shaped nano-islands dominate the deposits although spherical NPs are also present to a lesser extent. The nano-islands strongly resemble the structure typically formed as a result of atomic silver deposition onto weakly interacting substrates.^{23–25} At remote distances with $x > 39$ mm, spherical NPs start dominating again, yet the total NP number becomes smaller.

These findings are further supported by the longer 60 s deposition. At $x < 3$ mm, large amount of large NPs is deposited on the substrate forming a mesoporous deposit. The NPs are strongly coalesced similar to those found on the target surface, although their size is smaller. The strong coalescence may serve as evidence that the NPs have a temperature which is above or not very far below the melting point during their deposition onto the substrate. At $3 < x < 39$ mm, the formation of a discontinuous film with inclusions of spherical NPs is observed whereas the film growth is suppressed at $x > 39$ mm. Here, only spherical NPs are collected on the substrates and their coalescence becomes less obvious, suggesting that the NPs effectively thermalize on their travel along the aggregation chamber.

The analysis of the deposits confirms that Ag NPs escape from the capture zone both in the axial and in the radial direction. The sputtered atomic metal flux is in sufficient excess to be consumed in the gas phase for the NP formation as well as to reach the walls near about the magnetron and to contribute to the growth of films thereon. As a consequence, non-negligible amount of sputtered material is lost at the walls of the GAS instead of being transported in the form of a NP beam into the deposition chamber.

4. Discussion

After the ignition of the discharge, the NPs nucleate and grow in size to the average value of about 90 nm in the near-to-magnetron region, with the NP concentration reaching maximum at $x = 2.2$ mm. The NPs of this size can be found, yet only sporadically, on substrates positioned

outside the GAS in the main deposition chamber; however, they can be found more abundantly on substrates positioned inside the GAS close to the magnetron as well as on the magnetron target itself, in its central area. The behavior agrees with the earlier reported concept of the capture zone which is created at the several mm distance above the magnetron and circumscribed by a plasma ring. Smaller NPs have a higher probability to escape the capture zone and to constitute a beam of NPs travelling along the GAS with the gas flow. Larger NPs are trapped more effectively and therefore proceed growing further until they reach a critical size at which they become expelled from the capture zone and deposit on the adjacent surfaces.

The phenomenon of capturing/expelling is evidently governed by the balance of forces acting on the NPs, and this balance can be shifted depending on the NP size. Given that the majority of the NPs are negatively charged in the plasma, the following forces should be taken into account: the electromagnetic force (with the electric and magnetic components of the Lorentz force describing the movement of the NP upon the action of the electric and the magnetic field), the thermophoretic force (given by the temperature gradient if such exists in the space surrounding the NPs), the gravity, the neutral drag force (the force produced onto the NP by the momentum transfer from the neutral atoms constituting the gas flow) and the ion drag force (the force induced onto the NP by the momentum transfer from directed fluxes of ions). Scheme 2a demonstrates these forces acting on a negatively charged NP located at the inner periphery of the plasma ring and at the edge of the capture zone. The schemes were constructed on the basis of the simulations of the gas flow in the GAS as well as on the previous results of the Langmuir probe measurements (see Supporting information).

The collective action of the forces onto NPs may give rise to instabilities often observed in dusty plasmas.²⁶ The oscillations of the SAXS signal with the frequency of 1 Hz reported here strongly remind the so-called heartbeat instabilities that occur with the several Hz frequency in low-temperature dusty plasmas and comprise the cycling contractions and expansions of a particle-free region called a void.^{27–29} The underlying physics involves the formation and collapse of a sheath at the void boundary, the phenomenon given by the cycling accumulation of charge by dust particles and subsequent electrostatic expelling of critically charged NPs from the void.³⁰ In non-magnetized discharges with the parallel-plate electrode configuration, the particle-free void is formed in the central region of the particle cloud.²⁹ Our findings, both shown here and

reported earlier,¹⁹ indicate that the reverse is true for the magnetron discharge: the NPs concentrate in the central region and become periodically expelled therefrom (Scheme 2b).

Another possible explanation for the observed instabilities may include the rotation of the NP cloud about the magnetron axis. Such rotation may become possible if the tangential electric field appears within the circular plane of the cloud due to an inhomogeneous distribution of the NP charge (proportional to the NP size). This tangential component of the electric field may propel the NPs into a circular motion. If we interpret the time dependence of Fig.5 as the rotation of the trapped NP cloud, we can see that there is a sharp decrease of number density of the biggest NPs followed by a multitude of smaller NPs. This would correspond to the situation shown in Scheme 2b where the NP cloud is characterized by the tangential gradient of the NP size/charge. The cloud rotates about the magnetron axis, with the front of large NPs traversing the X-ray beam twice per period of the rotation.

Scheme 2 Illustration of two mechanisms that may be responsible for cycling instabilities observed by SAXS: a) cycling growth and expelling of NPs (larger NPs accumulate closer to the magnetron axis); b) axial rotation of the NP cloud (the NPs are tangentially separated by their size/charge, the entire cloud rotating clockwise). Top pictures show forces acting on a negatively

charged NP that is located at the inner periphery of the plasma ring and at the outer edge of the capture zone (only a quarter of the target is shown for simplicity), F_{el}^{rad} and F_{el}^{tg} are radial and tangential components of the electric force, F_{mag}^{rad} and F_{mag}^{tg} are radial and tangential components of the magnetic force, F_{th} is the thermophoretic force, F_n is the neutral drag force, F_{ion}^{rad} and F_{ion}^{tg} are radial and tangential components of the ion drag force. The gravitational force is not shown for simplicity.

At present, we are not able to distinguish which of the mechanisms (cycling growth/expelling or rotation of the NP cloud) is responsible for the observed instabilities. In fact, they need not be necessarily mutually exclusive and may probably co-exist to a certain extent. The NPs can definitely grow from 20 nm to 80 nm in 1s as witnessed during the initial stages of the process (Fig.3). This growth dynamics manifests itself at the timescale comparable to the period of the oscillations observed later (Fig.5). Actually, local spontaneous inhomogeneity in the NP growth can be a starting point for the instabilities to occur. Since the material must be arriving into the trapped cloud region during the entire power-on period, the NPs must grow inside the cloud at least to some extent. As a result, the apparent periodic changes in the NP size and density can be a superposition of the physical movement of the NPs with their (quasi)continuous growth. The smallest NPs are continuously replenished into the capture zone from the area above the erosion track and the biggest NPs continuously escape from the trap (Fig.8). We can name this process a growth-transport instability. Such “coupled processes” instability can be actually an interesting analogue of the ionization-movement instabilities observed as fast “spokes” in closed-drift ($E \times B$ drift) devices such as magnetrons^{31–33} or Hall thrusters^{34,35} but at a much longer timescale. However, we should admit that details of these phenomena remain unclear at present and require further investigation.

The cycling instabilities eventually subside and the system enters the steady-state regime. It is worth mentioning that the phenomenon of the postponed stabilization of the generation of NPs does not seem to be unique. It bears similar features to the earlier reported uncontrollable drift of the heartbeat frequency that occurred with submicron particles in dusty plasma at longer time intervals even though the experimental parameters were carefully maintained constant.³⁰

Conclusion

The kinetic processes of the synthesis of Ag NPs in the magnetron-based gas aggregation cluster source were analyzed by *in situ* and time-resolved SAXS measurements. The existence of the capture zone was confirmed in which the charged NPs are held mainly by electrostatic interactions. The capture zone is localized at 1 – 10 mm distance from the surface of the target and circumscribed by the magnetron plasma ring. The first NPs are found to appear within tenths of a second after the ignition of the discharge. The partial pressure of atomic Ag vapours does not limit the growth of the NPs, and they increase in size similarly fast at different axial distances from the target. After the initial period of the fast growth, the SAXS measurement detected the regime of cycling oscillations of the NP size and number which can be given by the combination of two mechanisms: 1) periodic expelling of NPs from the capture zone after they reach the critical size and 2) the rotation of the NP cloud about the magnetron axis. The oscillations of the SAXS signal eventually subside and the synthesis of the NPs enters the steady-state regime. Here, a constant amount of the NPs escape the capture zone and travel along the aggregation chamber with the velocity of the carrying gas. On their way to the exit orifice, a part of the NPs becomes lost on the inner walls of the chamber while another part becomes re-deposited from the capture zone back onto the surface of the target. The significant loss of the material within the aggregation chamber suggests that optimization of magnetron-based cluster sources is the question of high importance.

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