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Fast growth of nanoparticles in a hollow cathode plasma through orbit motion limited ion collection

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Plasma-based nanoparticle synthesis techniques are attractive in many respects but suffer from a major drawback—low productivity. We demonstrate a technique by which the growth rate of copper nanoparticles has been substantially increased by collection of copper ions. A growth rate as high as 470 nm/s was obtained as compared to a growth rate of less than 3 nm/s in the case of growth by neutrals. The increased trapping of copper is explained as orbital motion limited (OML) collection of ions. Experimentally obtained nanoparticle growth rates are in good agreement with theoretical estimates of the OML ion collection rates. © 2013 AIP Publishing LLC.

Nanoparticles have specific properties that are tunable by their size and shape, which can be leveraged to optimize surface properties. Plasmon resonance, for instance, is a function of both size and shape. One important application of plasmonic effects in nanoparticles is to enhance light trapping in solar photovoltaic cells leading to higher efficiency. In semiconducting nanoparticles, the band gap—which is a function of the size—is desirable to control and optimize, e.g., next generation high efficiency flat panel light emitting devices. For applications such as those mentioned above, the nanoparticles should ideally be deposited in a well separated manner upon the substrate in order to maintain their single particle properties.

Wet-chemical synthesis methods are known to generate nanoparticles with well controlled size and shape. Common techniques to deposit them upon a substrate are spin coating and spray coating. However, with these methods, it is difficult to distribute them so that they are well separated and non-agglomerated. An option is to use capping agents which can prevent agglomeration already in the solution; however, capping layers can affect the surface contact between nanoparticles, or between nanoparticles and the substrate surface, or the layer embedding them. This can have undesired effects both on the properties of the nanoparticles and on the interaction between them and the layer.

A different approach is to deposit the nanoparticles directly from the gas phase onto a surface. One such technique is flame synthesis, where it has been shown that large quantities of nanoparticles can be deposited directly onto a sensing unit. However, with flame synthesis, both control of the nanoparticle size and avoidance of agglomeration are sophisticated tasks. Better size control, and also a very good suppression of agglomeration in the gas phase, can be obtained with plasma-based processes; the agglomeration of nanoparticles is suppressed since nanoparticles become negatively charged within a plasma environment and repel each other. Plasma-based production of size-controlled nanoparticles with narrow distributions and different shapes has been demonstrated by several authors. The range of materials that can be synthesized by plasma-based gas phase synthesis methods is manifold, as both physical and chemical vapor deposition can be used, and nanoparticles have been made of materials ranging from carbon, silicon, metals, and oxides to nitrides. However, Bouchoule pointed out that particle growth in low-pressure plasma conditions cannot be easily managed for the production of material in large quantities. One important bottleneck is the reduced growth rate of the nanoparticles beyond the size where they have become negatively charged; further growth by coagulation is then suppressed, leaving slower growth by accretion of individual atoms and ions. Slow growth results in two closely connected problems which are a low productivity of the nanoparticles themselves and a poor utilization of the material out of which they form. With low capture efficiency on nanoparticles, material will (to a larger degree) be lost to the walls and boundaries including the substrate on which the nanoparticle deposition is to be made.

In this contribution, it is shown that the nanoparticle growth rate can be substantially increased by creating a highly ionized plasma and dynamizing growth by collecting ions rather than atoms. In so doing, the material available for growth is also consumed more efficiently.

Orbit motion limited (OML) collection of ions. The growth of nanoparticles is schematically illustrated in Figs. 1(a) and 1(b). The initial growth of a nanoparticle by nucleation, cluster formation, and aggregation, up to a size of about 10 nm diameter, is shown in Fig. 1(a), and further growth under conditions, such that electric attraction towards the nanoparticle has a large effect on the ion collection rate, is illustrated in Fig. 1(b). We will herein call this as OML collection since the theory needed to quantify the mechanism is
found in classical OML theory for spherical probes.\textsuperscript{30} When OML theory applies, the ion collection current to a spherical object varies with the potential as

\[ I_i = q_i n_i v_\text{th,i} \sigma_0 \left( 1 - \frac{V_{\text{NP}}}{k_B T_i / e} \right), \quad (1) \]

where \( q_i \) is the ion charge, \( m_i \) is the ion mass, \( n_i \) is the ion density, \( T_i \) is the ion temperature, \( e \) is the elementary charge, \( k_B \) is the Boltzman constant, \( v_\text{th,i} = (8 k_B T_i / (\pi m_i))^{1/2} \) is the average thermal speed of the ions, \( \sigma_0 = \pi r_{\text{NP}}^2 \) is the cross section of the nanoparticle (with radius \( r_{\text{NP}} \)) for collecting neutrals (which are not influenced by the potential) and the potential of the nanoparticle including sign. For grains larger than 10 nm (as we will study here), we assume that \( V_{\text{NP}} \) approximately equals the floating potential \( V_f \), at which ion and electron currents from the plasma to the nanoparticle balance each other. The floating potential is obtained from OML theory\textsuperscript{31} as \( V_f = -K (k_B T_e / e) \). This is inserted into Eq. (1) to give

\[ I_i = q_i n_i v_\text{th,i} \sigma_0 \left( 1 + K \frac{T_e}{T_i} \right). \quad (2) \]

The parentheses in Eq. (2) quantifies the increase of the effective ion collection cross section \( \sigma_{\text{eff}} \), as illustrated in Fig. 1(b), over the neutral collection cross section \( \sigma_0 \). The factor \( K \) depends on three parameters:\textsuperscript{31} \( T_e, T_i, \) and \( m_i \). For copper, the factor \( K \) is estimated to be 2.58 for \( T_e / T_i \approx 100 \). With ions in thermal equilibrium with the process gas (\( T_i = 0.025 \) eV) and \( \sigma_0 \) for typical electron temperatures in the range of \( T_e = (1-3) \) eV, Eq. (2) gives \( \sigma_{\text{coll}} \geq (100-300) \sigma_0 \). This is two orders of magnitude larger than the collection cross-section of neutrals and illustrates the potential improvement if active OML collection can be realized in practice. Please note that although the enhancement in the collection cross-sections does not depend on the densities, the flux onto a nanoparticle does, see Eq. (1). This indicates that for achieving an enhanced growth by OML collection, the degree of ionization of the source material must be high.

In OML theory, the effective collection cross section can be ascribed to an effective radius \( r_{\text{eff}} = \sqrt{\sigma_{\text{eff}} / \pi} \) which corresponds to trajectories that lead to a grazing incidence of the ion on the nanoparticle, as illustrated in Fig. 1(b).

Equation (2) immediately gives \( \sigma_{\text{eff}} = \sigma_{\text{NP}}^2 (1 + K T_e / T_i)^{1/2} \). For OML theory to apply, the effective radius \( r_{\text{eff}} \) must be smaller than both the Debye length \( \lambda_D \) and the mean free path \( \lambda_{\text{coll}} \) for elastic ion-neutral collisions.\textsuperscript{32} Both conditions are satisfied, with typically more than an order of magnitude, for all cases reported in this work.

We are using a hollow cathode discharge which, in general, is known to provide a high degree of ionization,\textsuperscript{33} and apply high power pulses similar to high power impulse magnetron sputtering\textsuperscript{34} which has been shown to enhance the ionization of the sputtered species substantially as compared to direct current magnetron sputtering.\textsuperscript{35} A schematic view of the experimental arrangement is given in Fig. 1(c). For a detailed description, see Ref. 19. The base pressure was \( 4 \times 10^{-4} \) Pa, and the working pressure was set to 107 Pa at an argon flow of 90 sccm fed through the copper hollow cathode. Pulses with a peak current of 3 A, pulse width of 30 \( \mu \)s, and frequencies of 125 to 1100 Hz were studied. The nanoparticles were deposited on silicon substrates coated with a 200 nm thick titanium layer. The size of the substrates used was (1 \( \times \) 1) cm\(^2\) and they were positively biased at 10 V to improve the collection of nanoparticles.

It has previously been shown\textsuperscript{19} that the size of nanoparticles can be varied between 10 and 40 nm by adjusting only the electric pulse parameters—i.e., the frequency, the pulse length, and the pulse current amplitude—with the anode ring held at one constant position of \( z_{\text{AR}} = 45 \) mm measured from the hollow cathode. This variation in growth is explained in Ref. 19 to be mainly due to variations in the metal ion density, i.e., the value of \( n_i \) in Eq. (2). For example, a higher pulse current and/or pulse length gives a higher ion density \( n_i \) in each plume of plasma ejected out of the hollow cathode from an individual pulse, while a higher pulse frequency gives a higher ion density \( n_i \) due to overlap of the material ejected in subsequent pulses. We want to minimize such variations of the density \( n_i \) in the present contribution and instead isolate the effect of varying the electron temperature, see Eq. (2). To achieve this, we vary the anode ring position \( z_{\text{AR}} \) while keeping the electric pulse parameters constant. The idea is that the supply of source material (the density \( n_i \) from inside the hollow cathode should be only marginally influenced by the anode ring position, while the electron temperature becomes elevated in an adjustable volume between the anode ring and the hollow cathode.

The spatial—and temporal—growth of nanoparticles outside of the hollow cathode is schematically illustrated in Fig. 1(c). We consider Zone I as a “black box” where the nucleation process and coagulation take place. The anode ring position \( z_{\text{AR}} \) is varied between 30 and 60 mm (Zone II), measured from the hollow cathode orifice. We assume that the growth process within Zone I remains the same when varying the anode ring position within Zone II. In Zone II, the main mechanism for growth is an accretion of single ions and neutrals; nucleation is improbable (perhaps even impossible) because the vapor is no longer supersaturated while coagulation is prevented since all nanoparticles are sufficiently large—i.e., above 10 nm—to be negatively charged. By varying the position of the anode ring, the part of Zone II that has an elevated electron temperature (and therefore enhanced OML collection of ions) can be shortened or extended.
Scanning electron micrographs with the anode ring at a distance of 30 mm, 45 mm, and 60 mm at a pulse frequency of 700 Hz are shown in Fig. 2 together with size distributions (obtained from larger samples of micrographs). The size distributions are fitted to a lognormal distribution, and the synthesized nanoparticles have a spherical shape. There is a clear increase in size of the nanoparticles from 10 nm in diameter \( z_{AR} = 30 \text{ mm} \) to over 30 nm \( z_{AR} = 45 \text{ mm} \) to 40 nm \( z_{AR} = 60 \text{ mm} \) with increasing anode ring distances. These trends in size (and the standard deviations) are shown in Fig. 3(b), together with the corresponding data for the surrounding AR at \( z_{AR} = 30 \text{ mm} \) to over 30 nm \( z_{AR} = 45 \text{ mm} \) to 40 nm \( z_{AR} = 60 \text{ mm} \) with increasing anode ring distances. For a comparison between the experimental results and the growth by OML collection predicted by Eq. (2), a trend in size (and the standard deviations) are shown in Fig. 3(b), together with the corresponding data for the surrounding AR at \( z_{AR} = 30 \text{ mm} \) to over 30 nm \( z_{AR} = 45 \text{ mm} \) to 40 nm \( z_{AR} = 60 \text{ mm} \) with increasing anode ring distances. The result is calculated with the program reported in Ref. 36, where the dynamics of our pulsed discharge was modeled using a zero-dimensional model for the plasma chemistry and the expansion outside of the hollow cathode was investigated using a two-dimensional model. This gives a residence time in Zone II of 32 ms. Hence, the average growth rate becomes \( \Delta r_{NP} / \Delta t = 15 \text{ nm} / 32 \text{ ms} \approx 470 \text{ nm/s} \).

To benchmark the estimated value for the growth rate, we assume that the increase in growth rate is obtained by increasing the time that the nanoparticles are exposed to an elevated electron temperature in Zone II. The growth rate as a function of electron temperature is estimated combining Eq. (2) with the growth due to ion mass flow to a nanoparticle \( \frac{d r_{NP}}{d t} = I \times m_i / (q_4 \pi r_{NP}^2) \) giving

\[
\frac{d r_{NP}}{d t} = \frac{1}{4} \eta_{i,th,i} \frac{m_i}{\rho} \left( 1 + \frac{K T_e}{T_i} \right).
\]

For a numerical example, we take average values in Zone II from the model of Hasan et al.\(^{36}\) for the metal ion.
density, \( n_i = 3 \times 10^{18} \text{ m}^{-3} \), take the ions to be in thermal equilibrium with the background argon gas, giving \( T_e = 0.026 \text{ eV} \) and use the density for copper \( \rho = 8954 \text{ kgm}^{-3} \). With these values, inserted in Eq. (3), the growth rate becomes a function only of \( T_e \). This function is plotted in Fig. 4 and shows that the growth rate is extremely sensitive to variations in the electron temperature. Unfortunately, the plasma discharge part of the model in Ref. 36 is limited to the volume inside the hollow cathode and does not include any heating of the electrons between the hollow cathode and the anode ring; such heating is, however, apparent to the naked eye by the distribution of light emission from the discharge. We therefore turn the problem around and ask: what would \( T_e \) need to be when \( \varepsilon_{\text{AR}} = 60 \text{ nm} \) in Zone II, in order to give the experimentally estimated growth rate of 470 nm/s? The answer is obtained graphically in Fig. 4 as \( T_e = 1.7 \text{ eV} \). The results from the model inside the hollow cathode indicate that this is a realistic but somewhat high value: \( T_e \) is here higher than 1 eV during the pulse, drops off after the pulse and levels off at approximately 0.3 eV. An effect that is not included in the presented theoretical considerations is collisions of ions with the background gas. These collisions can lead to an enhanced ion current. Using the definition of a capture radius given by Galli, \( R \), collisions might play a role even in our case and may explain why a high growth rate at lower electron temperatures can be achieved.

Of greater importance than a perfect quantitative agreement regarding \( T_e \) is comparing the nanoparticle growth to that expected in Zone II without active OML collection and with the same density of sputtered material. This growth rate can be obtained from Eq. (3) by setting the electron temperature to \( T_e = 0 \) [this gives the grain potential zero in Eq. (1), and thus takes away the effect of electric attraction of the ions]. The neutral collection rate thus obtained is only 2.8 nm/s, almost two orders of magnitude below the experimentally obtained 470 nm/s. It is drawn as a dashed line in Fig. 4.

In conclusion, it has been demonstrated that the efficiency of nanoparticle growth by active OML collection of ions can be increased by approximately two orders of magnitude as compared to growth by collection of neutrals. This was shown by manipulating the length where the growth region is subject to a hot electron plasma, and thereby, active OML collection can take place. In our experiments, the growth rate of copper nanoparticles has been raised from below 3 nm/s to 470 nm/s by using OML collection of sputtered copper ions onto the nanoparticles. The key to this technique is a discharge arrangement such that the major fraction of the copper becomes ionized before collection on the nanoparticles, and in which the electron temperature can be kept high in the volume where the nanoparticles grow. This provides an attractive possibility to remedy the main drawback with plasma-based nanoparticle production, i.e., the low productivity.

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![Figure 4](image-url)

FIG. 4. Growth rate \( \frac{dN_p}{dt} \) as a function of the electron temperature \( T_e \) for growth by OML collection calculated for an average ion density of \( 3 \times 10^{18} \text{ m}^{-3} \). The growth rate by neutral collection (blue dashed line) is 2.8 nm/s. For the experimental observed growth rate of 470 nm/s (green dashed arrows) explained by OML collection, an electron temperature of 1.7 eV is needed.

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