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N.B.: When citing this work, cite the original article.

Original Publication:

Iris Pilch, Daniel Söderström, M I Hasan, Ulf Helmersson and N Brenning, Fast growth of nanoparticles in a hollow cathode plasma through orbit motion limited ion collection, 2013, Applied Physics Letters, (103), 19, 193108.

<http://dx.doi.org/10.1063/1.4828883>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-102853>

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Citation: [Applied Physics Letters](#) **103**, 193108 (2013); doi: 10.1063/1.4828883

View online: <http://dx.doi.org/10.1063/1.4828883>

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

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(Received 8 October 2013; accepted 18 October 2013; published online 6 November 2013)

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. [<http://dx.doi.org/10.1063/1.4828883>]

Nanoparticles have specific properties that are tunable by their size and shape,^{1,2} which can be leveraged to optimize surface properties.³ Plasmon resonance, for instance, is a function of both size and shape.^{4,5} One important application of plasmonic effects in nanoparticles is to enhance light trapping in solar photovoltaic cells leading to higher efficiency.³ In semiconducting nanoparticles, the band gap—which is a function of the size^{6,7}—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.^{8–11} Common techniques to deposit them upon a substrate are spin coating^{12,13} and spray coating.¹⁴ 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.¹⁵ 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^{16–20} and different shapes²¹ 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,^{18,22} silicon,^{23–25} metals,^{17,19,21} and oxides^{26,27} to nitrides.²⁸ However, Bouchoule²⁹ 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

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found in classical OML theory for spherical probes.³⁰ When OML theory applies, the ion collection current to a spherical object varies with the potential as

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

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, $v_{th,i} = (8k_B T_i / (\pi m_i))^{1/2}$ is the average thermal speed of the ions, $\sigma_0 = \pi r_{NP}^2$ is the cross section of the nanoparticle (with radius r_{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_{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 theory³¹ as $V_f = -K(k_B T_e / e)$. This is inserted into Eq. (1) to give

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

The parentheses in Eq. (2) quantifies the increase of the effective ion collection cross section σ_{eff} , as illustrated in Fig. 1(b), over the neutral collection cross section σ_0 . The factor K depends on three parameters: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 σ_0 for typical electron temperatures in the range of $T_e = (1-3)$ eV, Eq. (2) gives $\sigma_{coll} \geq (100-300)\sigma_0$. 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 $r_{eff} = \sqrt{\sigma_{eff}/\pi}$ which corresponds to trajectories that lead to a grazing incidence of the ion on the nanoparticle, as illustrated in Fig. 1(b).

FIG. 1. (a) Sketch of the initial growth of nanoparticles with collection cross section of neutrals σ_n . (b) Sketch of the collection cross section of ions σ_{eff} (active OML collection). (c) Schematic of the growth zones and the growth mechanisms. In Zone I, nucleation takes place and clusters grow to a size after which they become negatively charged. Due to the negative charge of nanoparticles, the effective collection cross section in Zone II is much larger leading to an enhanced accretion of ions.

Equation (2) immediately gives $\sigma_{eff} = r_{NP}^2 (1 + K T_e / T_i)^{1/2}$. For OML theory to apply, the effective radius r_{eff} must be smaller than both the Debye length λ_D and the mean free path λ_{coll} for elastic ion-neutral collisions.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,³³ and apply high power pulses similar to high power impulse magnetron sputtering³⁴ which has been shown to enhance the ionization of the sputtered species substantially as compared to direct current magnetron sputtering.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 4×10^{-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 μs , 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 $(1 \times 1) \text{ cm}^2$ and they were positively biased at 10 V to improve the collection of nanoparticles.

It has previously been shown¹⁹ 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 $z_{AR} = 45$ 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_{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_{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.

FIG. 2. Examples of SEM micrographs and calculated size distributions over a sample of micrographs for anode ring positions at 30 mm, 45 mm, and 60 mm. The size distributions are fitted to a log-normal distribution (red line). A clear increase in nanoparticle size is found.

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 ($z_{AR} = 30$ mm) to over 30 nm ($z_{AR} = 45$ mm) to 40 nm ($z_{AR} = 60$ 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 frequencies 500 Hz (a) and 900 Hz (c). For all three frequencies, the nanoparticle size increases when increasing the anode ring position. Only minor variations in the size of nanoparticles at the same anode ring positions but different frequencies are found, which can be related to the lower peak current used in these experiments. For anode ring positions z_{AR} up to about 45 mm, the diameter increases linearly and there may be a tendency towards a saturation of the nanoparticle size. Such saturation could be caused either by a depletion of source material—i.e., most material is converted to nanoparticles—or by a reduction of the ion density n_i at large distances from the hollow cathode, due to diffusion out of the growth region which makes nanoparticle growth slower.

Comparison to theoretical growth through OML ion collection. For a comparison between the experimental results and the growth by OML collection predicted by Eq. (2), it is assumed that the growth history above z_1 is independent of the anode ring positions—i.e., when the anode ring position is lowered from position z_1 to position z_2 ($z_1 < z_2$), the history of growth remains the same for all positions $z \leq z_1$. Furthermore, the growth below the anode ring is not

governed by OML collection and only a comparatively small growth rate (as compared to growth by OML collection) can take place, which will be quantified by theoretical considerations given below.

When the anode ring is moved from the highest position $z_{AR} = 30$ mm to the lowest position $z_{AR} = 60$ mm, the nanoparticle radius r_{NP} increases from 5 nm to 20 nm giving a size increase of $\Delta r_{NP} = 15$ nm. For an estimation of the growth rate $\Delta r_{NP}/\Delta t$, the residence time Δt of a nanoparticle in the region between $z_{AR} = 30$ mm and $z_{AR} = 60$ mm can be estimated by the velocity of the gas flow. The residence time is calculated by integrating the gas flow over the time in Zone II. 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 $dr_{NP}/dt = I \times m_i/(q_i \rho 4\pi r_{NP}^2)$ giving

$$\frac{dr_{NP}}{dt} = \frac{1}{4} n_i v_{th,i} \frac{m_i}{\rho} \left(1 + K \frac{T_e}{T_i} \right). \quad (3)$$

For a numerical example, we take average values in Zone II from the model of Hasan *et al.*³⁶ for the metal ion

FIG. 3. Mean nanoparticle size as a function of the anode ring distance at constant frequency of (a) 500 Hz, (b) 700 Hz, and (c) 900 Hz. The standard deviations of the size distributions are represented by error bars. The same trends are found with little variation in the size of nanoparticles synthesized at different frequencies.

density, $n_i = 3 \times 10^{18} \text{ m}^{-3}$, take the ions to be in thermal equilibrium with the background argon gas, giving $T_i = 0.026 \text{ eV}$ and use the density for copper $\rho = 8954 \text{ kg m}^{-3}$. 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 $z_{AR} = 60 \text{ mm}$ 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 model³⁶ 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,³⁷ 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

FIG. 4. Growth rate dr_{NP}/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 experimentally observed growth rate of 470 nm/s (green dashed arrows) explained by OML collection, an electron temperature of 1.7 eV is needed.

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.

The work was financially supported by the Knut and Alice Wallenberg Foundation through Grant No. 2012.0083 and the Swedish Research Council under Grant No. 2008-6572 via the Linköping Linneaus Environment LiLi-NFM. D.S. acknowledges financial support from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO Mat LiU # 2009 00971).

- ¹B. P. Khanal, A. Pandey, L. Li, Q. Lin, W. K. Bae, H. Luo, V. I. Klimov, and J. M. Pietryga, *ACS Nano* **6**, 3832 (2012).
- ²P. Albella, B. Garcia-Cueto, F. González, F. Moreno, P. Wu, T.-H. Kim, A. Brown, Y. Yang, H. O. Everitt, and G. Videen, *Nano Lett.* **11**, 3531 (2011).
- ³H. A. Atwater and A. Polman, *Nature Mater.* **9**, 205 (2010).
- ⁴S. Linic, P. Christopher, and D. B. Ingram, *Nature Mater.* **10**, 911 (2011).
- ⁵K. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, *J. Phys. Chem. B* **107**, 668 (2003).
- ⁶A. I. Ekimov, A. L. Efros, and A. A. Onushchenko, *Solid State Commun.* **56**, 921 (1985).
- ⁷A. P. Alivisatos, *J. Phys. Chem.* **100**, 13226 (1996).
- ⁸V. Iablokov, S. K. Beaumont, S. Alayoglu, V. V. Pushkarev, C. Specht, J. Gao, A. P. Alivisatos, N. Kruse, and G. A. Somorjai, *Nano Lett.* **12**, 3091 (2012).
- ⁹S. E. Skrabalak and Y. Xia, *ACS Nano* **3**, 10 (2009).
- ¹⁰M. Grzelczak, J. Pérez-Juste, P. Mulvaney, and L. M. Liz-Marzán, *Chem. Soc. Rev.* **37**, 1783 (2008).
- ¹¹J. Chen, B. Lim, E. P. Lee, and Y. Xia, *Nano Today* **4**, 81 (2009).
- ¹²P. Colson, R. Cloots, and C. Henrist, *Langmuir* **27**, 12800 (2011).
- ¹³L. Xu, R. G. Karunakaran, J. Guo, and S. Yang, *ACS Appl. Mater. Interfaces* **4**, 1118 (2012).
- ¹⁴A. Steele, I. Bayer, and E. Loth, *Nano Lett.* **9**, 501 (2009).
- ¹⁵A. Tricoli and S. E. Pratsinis, *Nat. Nanotechnol.* **5**, 54 (2010).
- ¹⁶D. Vollath, *J. Nanopart. Res.* **13**, 3899 (2011).
- ¹⁷V. Stranák, S. Block, S. Drache, Z. Hubicka, C. A. Helm, L. Jastrabík, M. Tichý, and R. Hippler, *Surf. Coat. Technol.* **205**, 2755 (2011).
- ¹⁸V. Bouchat, O. Feron, B. Gallez, B. Masereel, C. Michiels, T. V. Borghet, and S. Lucas, *Surf. Coat. Technol.* **205**, S577 (2011).
- ¹⁹I. Pilch, D. Söderström, N. Brenning, and U. Helmersson, *Appl. Phys. Lett.* **102**, 033108 (2013).
- ²⁰S. Pratontep, S. J. Carroll, C. Xirouchaki, M. Streun, and R. E. Palmer, *Rev. Sci. Instrum.* **76**, 045103 (2005).
- ²¹R. Werner, T. Höche, and S. G. Mayr, *Cryst. Eng. Comm.* **13**, 3046 (2011).
- ²²C. Arnas and A. A. Mouberri, *J. Appl. Phys.* **105**, 063301 (2009).
- ²³P. Shen, N. Uesawa, S. Inasawa, and Y. Yamaguchi, *J. Mater. Chem.* **20**, 1669 (2010).
- ²⁴A. Bapat, C. R. Perreys, S. A. Campbell, C. B. Carter, and U. Kortshagen, *J. Appl. Phys.* **94**, 1969 (2003).
- ²⁵P. Scheier, B. Marsen, and K. Sattler, *J. Appl. Phys.* **94**, 6069 (2003).
- ²⁶A. Marek, J. Valter, S. Kadlec, and J. Vyskočil, *Surf. Coat. Technol.* **205**, S573 (2011).
- ²⁷L. Dreesen, J. Colomer, H. Limage, A. Giguère, and S. Lucas, *Thin Solid Films* **518**, 112 (2009).

- ²⁸J. Tavares, S. Coulombe, and J.-L. Meunier, *J. Phys. D: Appl. Phys.* **42**, 102001 (2009).
- ²⁹A. A. Bouchoule, *Dusty Plasmas: Physics, Chemistry and Technological Impacts in Plasma Processing* (John Wiley & Sons, Chichester, 1999), Chap. 4.
- ³⁰J. Allen, *Phys. Scr.* **45**, 497 (1992).
- ³¹M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, 2nd ed. (John Wiley & Sons, Hoboken, New Jersey, 2005), Chap. 17.2, pp. 651–653.
- ³²B. M. Annaratone, M. W. Allen, and J. E. Allen, *J. Phys. D: Appl. Phys.* **25**, 417 (1992).
- ³³V. I. Kolobov and L. D. Tseng, *Plasma Sources Sci. Technol.* **4**, 551 (1995).
- ³⁴V. Kouznetsov, K. Macák, J. Schneider, U. Helmersson, and I. Petrov, *Surf. Coat. Technol.* **122**, 290 (1999).
- ³⁵J. Bohlmark, J. Alami, C. Christou, A. Ehaszarian, and U. Helmersson, *J. Vac. Sci. Technol. A* **23**, 18 (2005).
- ³⁶M. I. Hasan, I. Pilch, D. Söderström, D. Lundin, U. Helmersson, and N. Brenning, *Plasma Sources Sci. Technol.* **22**, 035006 (2013).
- ³⁷F. Galli, “Charge and energy interactions between nanoparticles and low pressure plasmas,” Ph.D. dissertation (University of Minnesota, 2010).