

# High Power Pulsed Hollow Cathode for Nanoparticle Synthesis

Daniel Söderström<sup>1</sup>, Iris Pilch<sup>1</sup>, Nils Brenning<sup>2</sup>, and Ulf Helmersson<sup>1</sup>

<sup>1</sup>Linköping University, Plasma & Coatings Physics, Linköping, Sweden

<sup>2</sup>Royal Institute of Technology, School of Electrical Engineering, Division of Space & Plasma Physics, Stockholm, Sweden

## Abstract

Copper nanoparticles were synthesized using a novel method based on sputtering material from a hollow cathode using high power pulses. The high power pulses provide a supersaturated vapor with a high degree of ionization from which the nanoparticles are formed in the gas phase. By adjusting the pulse parameters, the plasma environment and thus the nanoparticle growth can be affected. It was found that the nanoparticle size can be influenced by varying, e.g., the pulse frequency or the pulse power. The results using the high power pulsed hollow cathode are compared to nanoparticles synthesized with a dc discharge using the same setup.

## Introduction

The large interest in materials in the form of nanoparticles (NPs) stems from the unique properties they have compared to bulk quantities, e.g. high surface-to-volume ratio [1,2] and plasmonic effects [3,4]. This has led to a demand for NPs with well-defined characteristics, e.g. sizes with narrow size distributions. The challenge is to develop a technique that can meet the demands. Today, there exist several techniques to synthesize NPs, e.g. milling, wet chemistry, flame synthesis, and plasma-based methods. Plasma-based methods provide an elegant method to create non-agglomerated NPs from a wide selection of materials in a controlled environment. The material from which the NPs should be synthesized can in the plasma-based methods be provided either chemically, i.e. in a reactive process [5], or physically in a sputtering process [6]. Using a physical method, any material that can be sputtered can in principle be used to synthesize NPs.

NPs in a non-equilibrium plasma will, when they reach a size of about 10 nm, be negatively charged due to the higher mobility of the electrons compared to the positive ions. This is the reason why the NPs will not be agglomerated in the plasma, which is a large benefit.

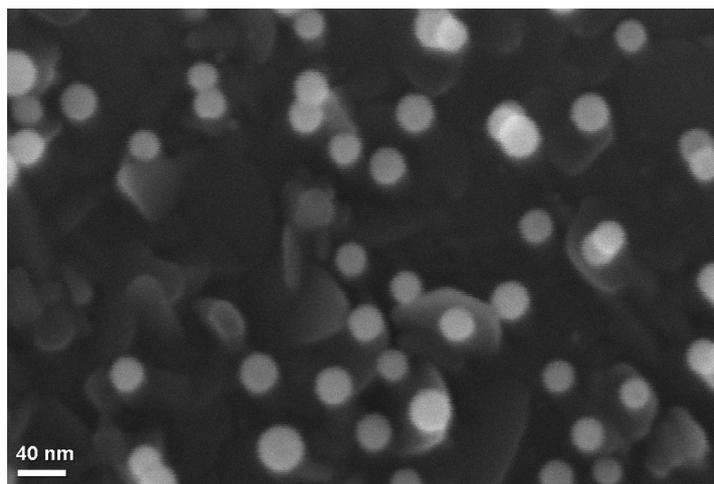
The NPs form in the plasma by a supersaturated vapor. Three-body collisions form small clusters that grow by colliding with each other or with single atoms or ions. As the NPs grow, they get negatively charged and coalescence between NPs is prevented. They can now only grow by collecting atoms or ions. Due to the attractive force between positive ions and the negatively charged NPs, the collision cross-section for positive ions is at least one order of magnitude larger than for neutrals. It is therefore of benefit to have a large fraction of the NP building material in ionized form. Achieving a high plasma density also leads to a higher density of sputtered material, which promotes NP formation.

In our novel method to synthesize NPs, we use high power pulses similar to what is used in high power impulse magnetron sputtering [7], to achieve a high plasma density. To further enhance the plasma density and to keep the plasma focused, we use a hollow cathode.

In this study, we have used a copper hollow cathode to synthesize copper NPs, and studied the effect of pulse power and pulse frequency on the size of the NPs. The results from the pulsed power method has also been compared to the results from running the same set-up with DC power.

## Method

The copper hollow cathode (length 54 mm, outer diameter 12 mm, and inner diameter 5 mm) was mounted at the center of the top lid of a stainless steel chamber with a diameter of 290 mm and a height of 430 mm. A sketch of the setup can be seen in figure 2. The cathode is water cooled with a gas inlet from above. Outside the orifice of the hollow cathode a stainless steel grounded anode shaped as a ring with a diameter of 30 mm is placed. The anode ring was kept at a distance of 45 mm from the cathode during the experiments. A volume outside the hollow cathode, including the anode ring, is enclosed by a stainless steel mesh cage that prevents the plasma from escaping to other grounded structures.



*Figure 1: Example scanning electron microscope image of copper nanoparticles. The background shows the titanium film on the silicon substrate.*

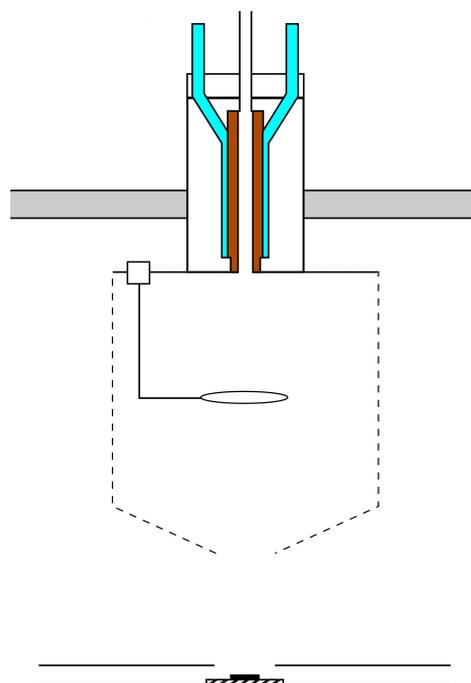
Below and outside the mesh cage, 160 mm from the hollow cathode, a rotatable substrate table with space for up to six substrates is mounted. The substrates are 10x10 mm silicon pieces with a 200 nm layer of titanium on them. To attract the negatively charged NPs to the substrates, a bias voltage of +10 V was applied to the substrates by a clamp to the substrate surface.

The chamber was pumped down by a turbomolecular pump backed by an oil-sealed pump to a base pressure of  $4 \times 10^{-6}$  Torr. Argon was used as sputtering gas, and the working pressure was set to 0.8 Torr (107 Pa), yielding an argon gas flow of 60 sccm. The high power pulses were delivered by a pulsing unit built in-house, fed by a DC power supply (Advanced Energy MDX-1K).

The dependence on the pulsing parameters were studied by varying the pulse frequency while keeping the pulse power (i.e. the energy per pulse) constant, and by keeping the time-average power constant, i.e. by decreasing the pulse power as the frequency is increased. The effect of varying pulse power was studied by keeping the frequency constant and equal to 700 Hz.

A series of experiments with DC power were also performed and compared to the pulsed power results. The setup during the DC experiments was the same as during the pulsed power experiments.

The synthesized NPs, collected on the titanium-coated silicon pieces were analyzed using a scanning electron microscope. An example of spherical copper NPs synthesized with the pulsed power process is shown in figure 1. Micrographs at different magnifications were run through a Matlab script which identified single NPs and calculated their size distributions. The mean size and standard deviation were calculated by fitting a log-normal distribution to the result.



*Figure 2: Schematic drawing of the experimental setup. Ar sputter gas flows through the hollow cathode, which is cooled by circulating water. The anode ring, mesh cage, and substrate table are seen below the hollow cathode.*

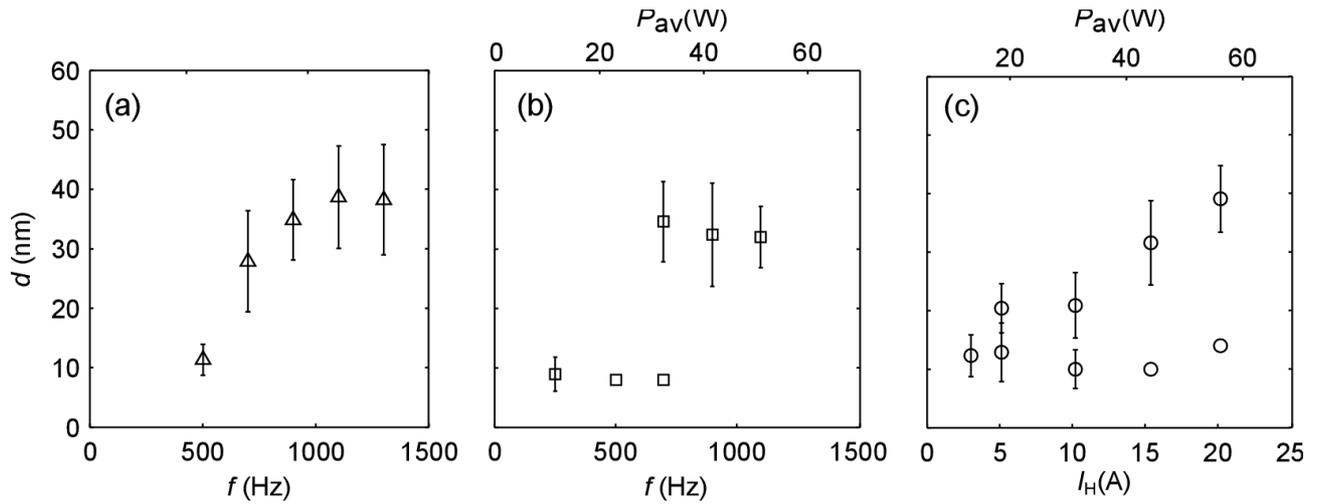


Figure 3: Mean nanoparticle diameters synthesized with the pulsed hollow cathode at (a) constant average power (30 W), (b) constant energy per pulse, and (c) constant pulse frequency ( $f=700$  Hz). The error bars indicate the standard deviation of the fitted log-normal distribution. Points without error bars did not have enough statistics to estimate a standard deviation.

### Results and discussion

The results from the pulsed power experiments are shown in figure 3. The NP size increases both with frequency and average power.

A step can be seen in the NP size when the frequency is increased with constant pulse power (the peak current in the pulse was kept at  $I = 10$  A) in figure 3 (b). Assuming that the sputtered material per pulse is the same, the increase in NPs size with frequency can be explained by an overlap of material and plasma from consecutive pulses. Since the shape of the current curve is constant when the frequency is changed, a plasma overlap within the hollow cathode can be excluded. Even when the frequency is changed with constant average power (figure 3 (a)) the NP sizes increases. As the frequency is increased the power per pulse, and thus the amount of sputtered material and the

ionization per pulse, is lowered to keep the average power constant. This shows that the material and plasma overlap is important, since sputtered material that is refilled to a region where NPs already exist mainly attaches to the NPs rather than form new NPs and a re-ionization by consecutive pulses charges already present NPs which can grow by the effect discussed in the introduction.

As the peak current in the pulses was changed at constant frequency ( $f=700$  Hz), two size populations could be observed, see figure 3 (c). The amount of smaller NPs decreased as the peak current increased. Since the frequency, 700 Hz, is in the range where a sharp rise in NP sizes occurs, it is natural that we have two size populations of smaller and larger NPs. As the peak current, and thus the power in the pulse, increases, more material is sputtered and the ionization degree increases, which increase the NP sizes.

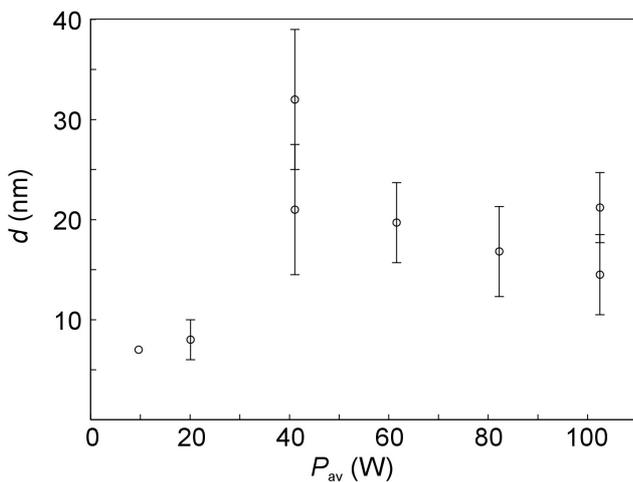


Figure 4: Mean nanoparticle diameters synthesized with the DC hollow cathode at different discharge powers. The error bars indicate the standard deviation of the fitted log-normal distribution. Points without error bars did not have enough statistics to estimate a standard deviation.

When the process was run with DC power, the synthesized NPs were generally smaller compared to the pulsed process at the same average power, as can be seen in figure 4. The size has a maximum around 40 W and decreases towards higher power. This has also been seen in other studies [8]. The NP formation is dependent on the surrounding gas temperature, and an elevated gas temperature is expected to heat the NPs so that they evaporate and are reduced in size. Since the gas temperature in the discharge would increase with deposited power, a reduction of NP sizes should be seen as the power is increased.

In the DC case we lack the effect of providing material at high density in pulses, and the degree of ionization should be lower compared to the pulsed case. Judging from the results of the pulsed process, where those two parameters are important, the continuous power deposition in the DC case leads to a different type of NP growth. The reduction of NP sizes as the average power is increased can not be seen from the results for the pulsed process. More experiments are needed to fully understand this process.

## Summary

A novel plasma-based NP synthesis process utilizing high power pulses has been developed. The high power pulses were applied to a copper hollow cathode, which leads to a high density plasma and a high sputtered material density. The pulse parameters frequency and pulse energy were varied. It was found that the NP sizes generally increase with average power. The same trend was seen for constant average power when the frequency was increased, showing that overlapping pulses are important for the NP growth.

The pulsed process was compared to a DC process using the same experimental setup. The results from the DC experiments show that the NP size in this case in general are smaller than the NPs synthesized by the pulsed process at the same average power. The sizes also show a maximum at a certain power with decreasing sizes towards higher powers, which can be caused by an increasing gas temperature at higher powers leading to a higher evaporation rate of the NPs.

## References

- [1] B. R. Cuenya, *Thin Solid Films* 518, 3127, 2010.
- [2] A. Z. Moshfegh, *Journal of Physics D: Applied Physics* 42, 233001, 2009.
- [3] S. Linic, P. Christopher, et al., *Nature Materials* 10, 911, 2011.
- [4] E. A. Coronado, et al., *Nanoscale* 3, 4042, 2011.
- [5] M. Adachi, et al., *Journal of Nanoparticle Research*, vol. 5, no. 1/2, pp. 31-37, Apr. 2003.
- [6] K. Ostrikov and A. B. Murphy, *Journal of Physics D: Applied Physics*, vol. 40, no. 8, pp. 2223-2241, Apr. 2007.
- [7] U. Helmersson, et al., *Thin Solid Films* 513, 1, 2006.
- [8] K. Ishii, K. et al., *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 17, no. 1, p. 310, 1999.