Synthesis of Copper Nanoparticles by a High Power Pulse Hollow Cathode

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ABSTRACT

A novel plasma-based nanoparticle synthesis method was used for synthesizing copper nanoparticles. High power pulses were applied to a cylindrical hollow cathode providing a high density and a high degree of ionization of the sputtered material. The variation of the nanoparticle size distributions were analyzed from scanning electron microscopy images and studied with respect to varied pulse parameters, e.g., pulse width and peak current. It was found that the nanoparticle size can be changed in a range between 10 and 40 nm by varying the pulse parameters.

Keywords: nanoparticle, hollow cathode, sputtering, plasma, pulsed power

1 INTRODUCTION

Material in the form of nanoparticles have unique properties that are absent at bulk quantities, e.g., high surface to volume ratio [1,2] and plasmonic effects [3,4]. The challenge today is to be able to create unagglomerated nanoparticles with narrow size distributions in sufficient amounts for different applications. There are many existent techniques to synthesize nanoparticles, e.g., milling methods, wet-chemistry, flame synthesis, and plasma-based methods. Plasma-based methods can be divided into two categories with respect to the mechanism which provides the source material. The material can be provided chemically, i.e., reactive processes [5], or physically by sputtering the material from a target. Using a physical vapor condensation technique, e.g., magnetron sputtering [6], has the benefit that any material, which can be sputtered, can in principle be used to synthesize nanoparticles. Another benefit with the plasma-based methods is that the nanoparticles attain a negative charge ─ when exceeding a specific size (~10nm) ─ which impedes agglomeration of nanoparticles in the gas phase.

A simplified description of the nanoparticle formation in the gas phase includes three stages of growth. In the first stage, dimers are formed from a supersaturated vapor by three-body collisions. Next, the dimers grow by collisions with single atoms and ions, and coalescence with other dimers and clusters of a few atoms. In the last step, the nanoparticles become negatively charged and the growth by coalescence is impeded, since the nanoparticles repel each other. Now, the growth can only proceed by the collection of single atoms or ions. The cross-section for collisions with positive ions is at least one order of magnitude larger than the collision cross-section for neutrals, which makes the collection of positive ions much faster than of neutrals. To enhance the nanoparticle growth, it is therefore desirable to increase the ionization degree as it is expected that this will enhance the nanoparticle growth. A high ionization degree will also lead to more sputtering which promotes cluster formation due to the high density of sputtered material.

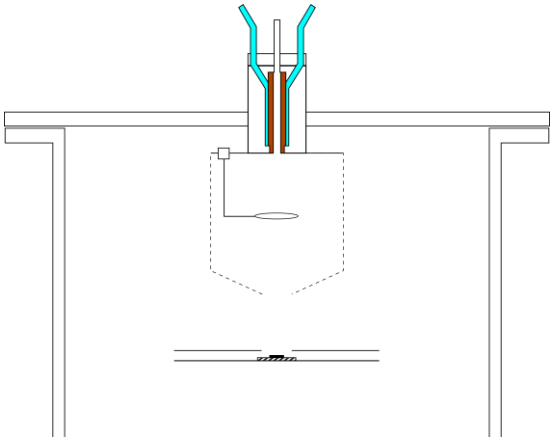

Figure 1: A schematic of the experimental setup. The water-cooled hollow cathode (red) is fed with Ar sputter gas from above. Below the cathode an anode ring is attached. A mesh cage was used to confine the nano-particles to the substrate table.

To achieve a highly ionized plasma, short high power pulses similar to what is used in high power impulse magnetron sputtering [7] can be applied to a plasma source. To achieve a high density of the sputtered material and to keep the plasma focused, a hollow cathode can be used for nanoparticle synthesis.

In this contribution, a novel technique for synthesizing nanoparticles is presented. Nanoparticles were synthesized from a copper hollow cathode by applying short high power pulses. The size of the nanoparticles is studied with respect

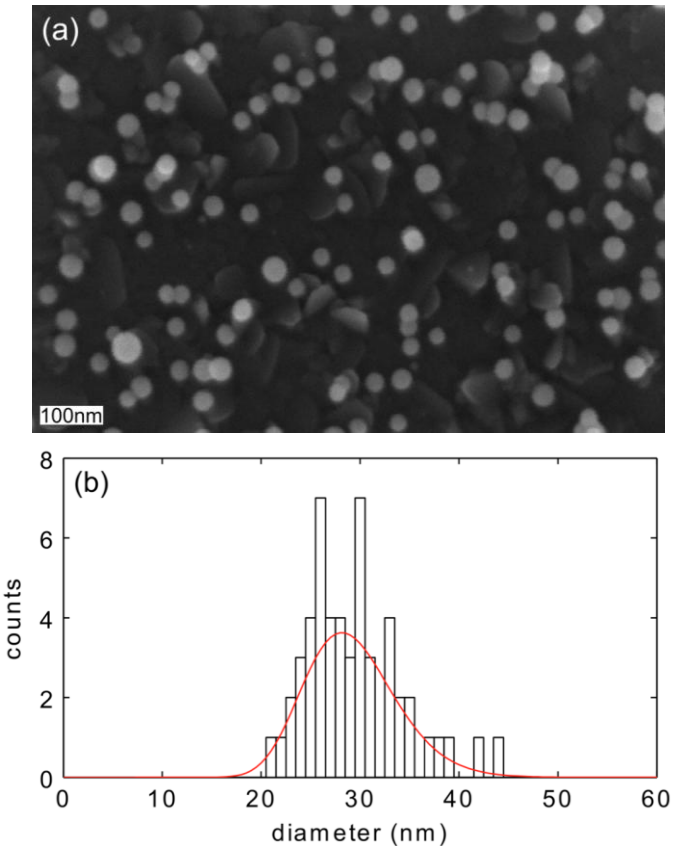

Figure 2: (a) Example of a scanning electron microscope micrograph of spherical nanoparticles, and (b) the corresponding size distribution calculated from the image. The structure of the titanium coated substrate can be seen as plates sticking out of the surface. The size distribution is fitted with a log-normal distribution (red line).

to the applied pulse parameters, i.e., pulse width and peak current.

2 EXPERIMENTAL TECHNIQUE

The experiments were done in a stainless steel cylindrical chamber with a 290 mm inner diameter and a length of 430 mm. A sketch of the setup is shown in Fig. 1. The hollow cathode is mounted at the center of the top lid, and is water-cooled. It has a length of 54 mm, an inner diameter of 5 mm and an outer diameter of 12 mm. A grounded anode made of a stainless steel wire in the form of a ring with a diameter of 30 mm is placed 45 mm below the cathode, and a mesh cage encloses the anode ring and the hollow cathode exit. The substrate table is 160 mm away from the cathode and six substrates can be loaded at the same time. The substrates are made of silicon with a 200 nm thick layer of titanium and have a size of 10x10 mm. In order to improve the nanoparticle collection on the substrates, a positive bias of 10V was applied to a clamp which was electrically connected to the substrate surface. The base pressure of the chamber was $4x10^{6}$ Torr. Argon

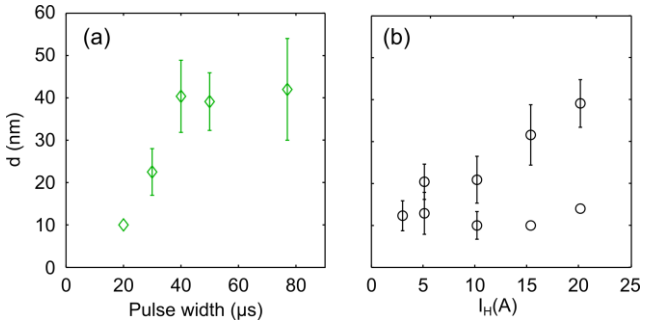

Figure 3: Dependence of the nanoparticle size on (a) the pulse width and (b) the peak current. The error bar denotes the standard deviation of the size distribution. For points without error bars, the statistics of the nanoparticles were too poor to fit a distribution.

was used as sputter gas at a pressure of 0.8 Torr (107 Pa) and at a flow rate of 60 sccm.

The pulsed power was supplied by a pulsing unit (own fabrications) fed by a DC power supply (Advanced Energy MDX-1K). The pulse was characterized by a frequency of 700 Hz, a pulse width of 10 to 77 µs and a peak current of up to 20 A. The parameter dependence was studied by varying one of the parameters and keeping the others constant. Standard parameters for synthesizing nanoparticles were: peak current I_H = 10 A, frequency f = 700 Hz, and pulse width t_{PW} = 30 µs.

The nanoparticles were collected on a substrate and analyzed using a scanning electron microscope. Micrographs were taken at different positions on the sample and for different magnifications. A Matlab program was used to calculate the nanoparticle size distribution from the micrographs. The mean size, i.e., the expected value, and the standard deviation were determined by fitting a log-normal distribution, and those values are used in the following to describe the change in particle size.

3 RESULTS AND DISCUSSION

Using the pulsed process developed, it is possible to vary the process condition over a wide parameter space by altering the repetition frequency, length of pulses and power of pulses. Here, the results from altering the pulse width [Fig. 3(a)] and the pulse power, which is a function of peak current, [Fig. 3(b)] are shown. In both experiment series a pulsing frequency of 700 Hz was used. The peak current was set to 10 A when varying the pulse width, and the pulse width for varying peak current was 30 µs. By varying one parameter, the average power changes as well.

It is found that the nanoparticle size increases with both increasing pulse width and peak current. The width of the size distribution increases for increasing pulse width but not when changing the peak current, i.e., the pulse power. In case of changing the peak current, two size populations were synthesized and the amount of the smaller population (~10 nm) decreases when the peak current is increased.

To relate the change in nanoparticle size – by varying the pulse parameters – with the mechanism of nanoparticle formation, the effect of the pulse parameters on the plasma parameters that are affecting the nanoparticle growth – e.g., temperature, densities, and ionization degree – need to be correlated. The gas temperature is a function of average power, i.e., with increasing average power the gas temperature should increase as well. For an elevated gas temperature the desorption of material from a nanoparticle increases which would lead to a decrease in nanoparticle size. Since no decrease with increasing average power has been found, an effect due to a change in temperature can be excluded and the change in density of sputtered material and the ionization degree are the important quantities to consider.

By varying the peak current, the amount of sputtered material and its ionization degree is affected. For increasing peak current, more material is sputtered and the ionization degree should increase as well. When varying the pulse width, the dependence of sputtered material and its ionization becomes more complex because the average power increases and also the rising time of the current curve changes. Nevertheless, the amount of sputtered material should increase for larger pulse widths. A variation in ionization degree is also expected and it possibly increases with larger pulse widths.

The influence of a higher ionization degree would affect the phase of nanoparticle growth when they are charged as the collection probability becomes larger. Thus, by only increasing the ionization degree but having the same density of sputtered material, an increase in nanoparticle size can be expected as long as the material is not fully consumed.

The increase of nanoparticle size with peak current and pulse width can also be related to an increase in density of sputtered material. A higher density can have two effects. First, it is possible that the density of growing nanoparticles, i.e., clusters, increases. Second, assuming that the number density does not change substantially, more material for nanoparticle growth is available and nanoparticles can become larger. The first case can also lead to larger nanoparticles as in the beginning of the growth, the clusters can grow by coalescence and the probability for coalescence increases with a higher density of clusters.

In the present study, it is not possible to distinguish which parameter has a bigger influence since the parameters could not be changed independently. To separate between the different possible mechanisms, further studies are needed. In addition to experiments, simulations can be a helpful tool for this task.

4 SUMMARY

A novel plasma-based nanoparticle synthesis method using high power pulses has been developed. A high power pulse, similar to high power impulse magnetron sputtering, was applied to a cylindrical hollow cathode, which leads to a high degree of ionization and a high density of the sputtered material.

The influence of pulse parameters, i.e., pulse width and peak current, on the synthesis of nanoparticles was studied. It was found that for both parameters the size of the nanoparticles increases. The width of the size distribution changes with pulse width but not with peak current. Two size populations were synthesized when changing the peak current and the amount of the smaller population became less for higher peak currents. Other experiments when varying the repetition frequency have shown that the appearance of the smaller nanoparticle population can be suppressed.

The increase in nanoparticle size can be understood by an increase of sputtered material and an increase in its ionization degree.

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