Computer simulation of the collection probability of ions and neutrals on nanoparticles in a plasma

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Plasma-based nanoparticle synthesis methods come in a variety of configurations. They all have in common that they are efficient techniques to generate nanoparticles with narrow size distributions of nearly any material. The narrow size distribution can be attributed to the electrostatic repulsion between nanoparticles in a plasma. When the nanoparticles grow to a certain size, they become negatively charged, if the electron thermal speed is larger than the ion thermal speed [1]. In this contribution, we focus on modeling the synthesis of nanoparticles in a sputtering source [2]. In most such sources, the sputtered material is to a large extent neutral [3], and the growth of the nanoparticles is slow. To utilize the negative charge of the nanoparticles to increase the growth speed, the sputtered material should be positively ionized, so that it is attracted to the nanoparticles.

A high degree of ionization of the sputtered material can be achieved with a hollow cathode in combination with high power pulses, similar to what is used in high power impulse magnetron sputtering [4]. A recent computer model of the discharge has shown that the sputtered metal ion density inside the hollow cathode reaches values of 10^{20} m^{-3} during the pulses [5].

A computer model was developed to understand how plasma parameters – such as electron temperature and plasma density – affects the collection of sputtered material on nanoparticles. The results from the model will help to guide the experiments to improve the efficiency in growing nanoparticles.

Theory

The nanoparticle growth can be divided in three stages: nucleation, coagulation, and accretion by attachment of single ions and atoms. Nucleation starts by a three-body collision which forms a dimer, which grow to larger clusters by colliding with each other as well as with single ions and atoms. As the number of single atoms and ions is reduced, the growth becomes dominated by coagulation between clusters, if not new ions or neutrals are supplied. As the clusters grow, they get negatively charged and coagulation abates due to repulsion. The nanoparticles can now only grow by single atom or ion attachment, which is a rather slow process if most of the material is neutral, since the cross section for collecting a neutral is the geometrical cross section $\sigma_{\text{geo}} = \pi a^2$, where a is the nanoparticle radius. Ions, on the other hand, are attracted to the negatively charged nanoparticles, and have a collection cross section larger than the geometrical cross-section. Assuming the orbital motion limited (OML) theory [7] can be applied, the maximum impact parameter a singly ionized ion can have and still be collected by a nanoparticle is

$$\rho_{\text{c,i}} = a\sqrt{1 - \frac{2e\phi_{\text{s}}}{mv^2}}, \tag{1}$$

where ϕ_{s} is the surface potential of the nanoparticle, m the ion mass and v its speed. The cross section for collection can then be written

$$\sigma_{\text{c,i}} = \pi \rho_{\text{c,i}}^2. \tag{2}$$

The surface potential can be calculated by equating the ion and electron current to the nanoparticle under the OML approximation [6],

$$\phi_{\text{s}} = -K\frac{k_{\text{B}}T_{\text{e}}}{e}, \tag{3}$$

with k_{B} the Boltzmann constant and T_{e} the electron temperature. K depends on the masses and temperatures of ions and electrons, but is assumed to be constant and equal to 2.5 in this work.

The electrostatic potential around the nanoparticles is needed to be able to calculate deflection angles in a collision event. Is is assumed that the Debye-Hückel potential can be used for small ($a = 10^{-8}$ m) nanoparticles [8],

$$\phi(r) = \frac{e}{4\pi\varepsilon_0 r}\exp(-r/\lambda_{\text{D}}), \tag{4}$$

where λ_{D} is the linearized Debye length.

Method

The model, written in Python, tracks a test particle that is either an ion or a neutral copper atom in phase space. The test particle is placed at the center of the simulation domain (a cube with a side of 30 mm) and is given a velocity sampled from a Maxwellian distribution with temperature $T_{\text{g}} = 300$ K. In each time step, the cross sections for a collision between the test particle and a plasma ion, a neutral atom or a nanoparticle (both collection and scattering) are calculated. A random number determines which collision occurs (a Monte Carlo collision scheme), and the scattering angle and new velocity is calculated. The test particle is advanced one step in space accordingly. All background particles (ions, neutrals, and nanoparticles) have a constant and homogeneous density. The electrons do not affect the test particle, but determine the nanoparticle charge and the electrostatic potential around the nanoparticle. The collisions with neutrals are modeled as hard sphere collisions. The modeling of ion-ion collisions do only take large angle scatterings into account, according to Spitzer [9].

Results and discussion

The simulation was run to obtain the probability of collecting an ion or a neutral test particle on a nanoparticle as a function of plasma density, neutral gas (argon) pressure, electron temperature and nanoparticle number density. The probability is determined from 100 test particles for each data point.

The collection probability of ions and neutrals as a function of neutral gas pressure is shown in Figure 1. It is found that the probability of collecting ions goes to 1 much faster with pressure than for neutrals. Since we are using the OML theory, the results might be inaccurate at higher pressures (> 10 Torr) due to collisions within the Debye sphere around the nanoparticle.

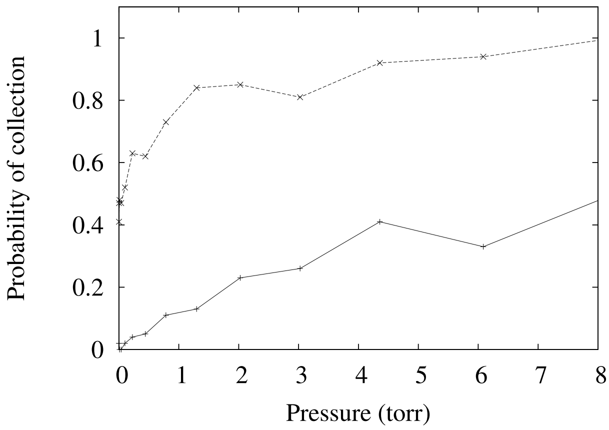

Figure 1: *Comparison of ion (dashed line) and neutral (full line) collection probability as a function of pressure. The lines are plotted to guide the eyes. The plasma density was set to* 10^{18} m^{-3}*, the electron temperature to 0.5 eV and the nanoparticle number density to* 10^{14} m^{-3}*. The nanoparticle radius was 10 nm.*

The probability of collection of ions as a function of electron temperature and plasma density is shown in Figure 2. The neutral gas pressure was held constant at 0.8 Torr (107 Pa) and the number density of the nanoparticles was set to 10^{14} m^{-3}. The red and green areas correspond to regions where less and more than 75% of the ions are collected, respectively. The curve dividing the areas shows a maximum around the plasma density 10^{18} m^{-3}. As the plasma density is increased, the path length of ions increases due to more frequent ion-ion scattering events, and the probability of hitting a nanoparticle increases. However, as the plasma density increases, the Debye screening of the nanoparticle also increases, leading to a smaller scattering cross section for ion-nanoparticle collisions. At low plasma densities the scattering on nanoparticles is important to increase the test particle path length, but at higher plasma densities the ion-ion scattering dominates. Since the neutral gas density is constant while the plasma density is increased, the neutral test particles are only affected by the increasing number of collisions with plasma ions, and are only collected to 11% at the highest plasma density.

The rectangle in Figure 2 indicates a range of probable values for the plasma outside the orifice of the hollow cathode used in experiments [2, 5], showing that an efficient use of the ionized sputtered material could be realized if the plasma density and the electron temperature are kept high.

It should be noted that also the neutrals could be collected to 100% if the neutral gas pressure is increased or if the geometrical size of the plasma is increased, due to a longer path length for the neutrals in the plasma. An increased neutral gas pressure would, however, imply a reduced discharge dimension, which would lead to less efficient collection of the sputtered material, and an increase in the size of the plasma is not practical.

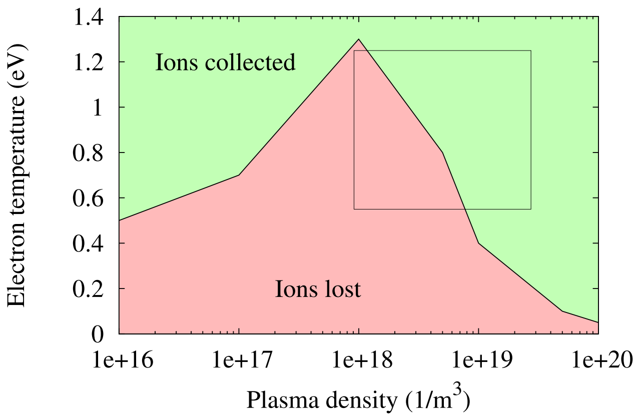

Figure 2: *The collection of ions as a function of the plasma density and the electron temperature. The green area indicates a collection of more than 75% of ion test particles. The rectangle indicates a region of probable parameters outside the hollow cathode used in the experiments. The nanoparticle number density was set to* 10^{14} m^{-3} *and the neutral gas pressure to 0.8 Torr (107 Pa). The nanoparticle radius was 10 nm.*

The computer simulation has provided us with a tool to help guide the experiments and has shown that the parameters used in the experiments lie within a range that ensures an efficient collection of ionized sputtered material.

References

[1] J. Goree, Plasma Sources Science and Technology, **3**, 3 (1994)

[2] I. Pilch, et al., Appl. Phys. Lett., **102**, 033108 (2013)

[3] C. Christou and Z. H. Barber, J. Vac. Sci. Technol. A **18**, 2897 (2000)

[4] U. Helmersson, et al., Thin Solid Films, **513**, 1–2 (2006)

[5] M. I. Hasan, et al., Plasma Sources Sci. Technol., **22**, 3 (2013)

[6] T. G. Northrop, Phys. Scri. **45**, 5 (1992)

[7] J. E. Allen, Phys. Scri. **45**, 5 (1992)

[8] V. Fortov, et al., Phys. Rep., **421**, 1–2 (2005)

[9] L. Spitzer, "Physics of fully ionized gases." Interscience Tracts on Physics and Astronomy, New York: Interscience Publication, 1965, 2nd rev. ed. 1 (1965).