# Growth processes of nanopartilces in processing plasmas and their control

プロセスプラズマにおけるナノ粒子の成長とその制御

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We review growth processes of nanoparticles in low pressure processing plasmas and display several growth control methods. Plasma nanoparticle technology can play core roles in "plasma nanofactory". One possible type of "plasma nanofactory" is 3D nanoprinting with parallel processing.

### **1. Introduction**

Among a great variety of nanotechnologies, nanoparticle technology is one of the central nanotechnologies [1-19]. Nanoparticle technology handles the preparation, processing, characterization and applications of nanoparticles, and it makes use of the unique properties of the nanoparticles that significantly differ from those of the bulk materials. Nanoparticle technology plays an important role in the implementation of nanotechnology in many engineering and industrial fields including electronic devices, advanced ceramics, new batteries, engineered catalysts, functional paint and ink, drug delivery system, biotechnology, sensors, solar cell,

hydrogen storage, etc. Various kinds of thermal and nonthermal plasmas in gases and above/in liquids have been employed for production of nanoparticles.

So far, we have studied nanoparticle growth kinetics in low-pressure processing plasmas [1, 7-21]. Based on the results, we have proposed the concept of "plasma nanofactory" which is a miniature version of a macroscopic conventional factory [8]. A plasma nanofactory produces nanoblocks and radicals (adhesives) in reactive plasmas, transports nanoblocks towards a substrate and arranges them on the substrate. We have developed several key control methods for a plasma nanofactory: size and structure control of



Fig. 1. Control of size of nanoparticles, their agglomeration, transport, and sticking.

nanoparticles, control of their agglomeration, transport and sticking, and then have demonstrated the combination of several types of control [8]. Figure 1 shows some examples of the control. Plasma offers agglomeration control without surfactant, directional transport of nanoparticles, and parallel processing.

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## 2. Nucleation

Here we focus on homogeneous nucleation. We must discriminate nucleation in low pressure nonthermal plasmas from that in thermal plasmas.

Nucleation in thermal plasmas can be described by classical theory of supersaturation. Rapid quenching, namely cooling gas temperature leads to supersaturation. Small particles (seeds) can trigger condensation of the vapor. Seeds triggering the conversation of vapor are referred to as condensation nuclei. Therefore concentration of source materials and gas temperature are key parameters to control the nucleation.

Nucleation in low pressure nonthermal plasmas is determined by two factors: one is dissipation of exothermic energy of polymerization reactions, and the other is electrostatic trapping of nuclei in plasmas. Since nucleation rate depends on radical density in a superlinear way, it also depends on plasma electron density in a superlinear way, that is, a slight increase in electron density leads to a significant increase in nanoparticle density.

Nucleation ceases in the high nucleation desnity case for which nuclei absorb most radicals, whereas successive nucleation takes place in the low nucleation density case. The former case brings about a short nucleation period and narrow size distribution, whiles the latter brings about a long nucleation period and wide size distribution.

# 3. CVD growth

CVD growth is growth of nanoparticles due to accretion of radicals on their surface. At low temperature of nanoparticle surface nanoparticles tend to grow spherically and have amorphous structures, whereas they tend to grow with euhedral surfaces and have crystal structures. In most cases, CVD growth rate is proportional to radical density and electron density. When most radicals are employed for such CVD growth of nanoparticles, the rate equation of radical density and that of nanoparticle growth rate form a closed loop, and hence these equations can have negative feedback and positive feedback with respect to perturbation of a parameter in the equations. Nonlinear behavior takes place in such closed loop case.

#### 4. Agglomeration

Aggregation and agglomeration are terms to refer to nanoparticles that have associated into a cluster composed of two or more nanoparticles. Agglomeration is caused by collision between nanoparticles, and the mono-disperse agglomeration rate is proportional to square of nanoparticle density. Ploy-disperse agglomeration behaves in more complex way.

#### 5. Conclusions

Plasma nanoparticle technology can play core roles in "plasma nanofactory". One possible type of "plasma nanofactory" is 3D nanoprinting with parallel processing.

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