Observation of nanoparticle growth process using a high speed camera

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Abstract: Time evolution of spatial profile of nanoparticle amount in low pressure reactive discharge plasmas have been measured to study effects of amplitude modulation of the plasmas on particle growth in the initial growth phase. Amplitude modulation of discharge voltage leads to oscillate nanoparticle amount and their spatial profile. Growth of nanoparticles is suppressed by increasing the AM frequency.

Keywords: nanoparticle, plasma-nano interface, plasma fluctuation, amplitude modulated discharge, laser light scattering

1. Introduction

Nanoparticle technology, which can be regarded as the extension of the conventional fine particle and powder technology, is one of the core nanotechnologies. This technology has a great potential in industrial and engineering areas such as catalysis [1-5], sensors [6], solar cell [7-9], hydrogen storage [10], Ultra-Large Scale Integration (ULSI) [11-13], hard coating [14], and biointerface [15]. Nanoparticle technology has many issues including control of size, strurture, agglomeration, morphology, surface, defect, dopant, and impurity of nanoparticles. One of the important and difficult issues of nanoparticles is to tune variations of such features of nanoparticles. Although spatial and temporal fluctuation of nanoparticle fabrication conditions leads to such variations, effects of fluctuations on such variations have not been clarified yet.

Up to now, we have carried out systematic studies on particle growth kinetics in a particle size range from sub-nm to μ m in low-pressure, high-frequency discharges employed for depositing Si thin films [16-23]. Based on the results, we have proposed the concept of 'nano-factory in plasma' which is a miniature version of a macroscopic conventional factory. A nano-factory in plasma 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 nano-factory in plasma: size and structure control of nanoparticles, control of their agglomeration, transport and sticking, and then explain the combination of several types of control [24-35].

Recently, we have studied effects of plasma fluctuation on growth of nanoparticles in reactive plasmas with amplitude modulation (AM) and clarified that plasma fluctuation leads to generation of high denisty of nanoparticles with small size [32].

In this paper, we report time evolution of spatial profile of nanoparticle amount measured using an in-situ two dimensional laser light scattering (2DLLS) method with a high speed camera and discuss effects of plasma fluctuation on nanoparticle growth in the initial growth phase.

2. Experimental Setup

Experiments were carried out using a capacitively-coupled discharge reactor equipped with a 2DLLS system as shown in Fig. 1 [32]. A powered disc electrode of 60mm in diameter and 1mm in thickness was set 20mm form an upper and lower grounded electrodes of 60mm in diameter. Ar diluted $Si(CH_3)_2(OCH_3)_2$

(DM-DMOS) was supplied to the reactor. The flow rate of Ar and DM-DOMS were 40 sccm and 0.2 sccm, respectively. The total gas pressure in reactor was 1.25 Torr. To generate nanoparticles, we sustained a discharge by applying 120 peak-to-peak voltage V_{pp} of 60MHz to the powered electrode for a discharge period T = 8s. The corresponding discharge power was 30W. Amplitude modulation of rf discharge voltage was carried out with a sinusoidal wave of a frequency f_{AM} of 10 and 20Hz. The AM level was 30%.

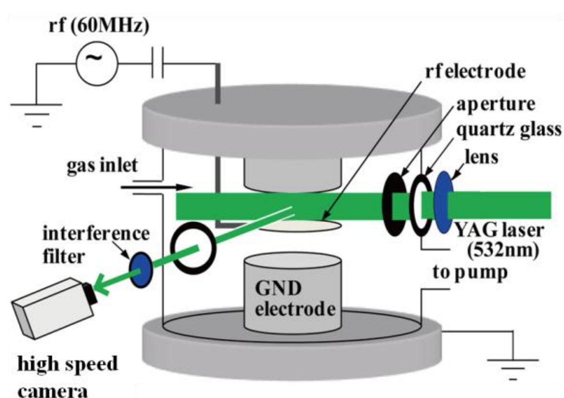

Fig. 1. Experimental setup.

Time evolution of spatial profile of LLS intensity from nanoparticles was measured using the 2DLLS method. For the 2DLLS method, a sheet beam of YAG laser light of 2.0W at 532nm was passed parallel to the surface of the upper grounded electrode through the aperture. The height and width of the sheet beam were 17mm and 3mm, respectively. Time evolution of spatial profile of LLS intensity was measured with a high speed camera (Photoron FASTCAM SA4) equipped with an interference filter of a center wavelength of 532nm and the full width at half maximum of 2nm.. The spatial resolution is 950 × 287 mm^2 and the frame rate is 1000 s^{-1}.

3. Results and Discussion

To obtain information on nanoparticle growth, we

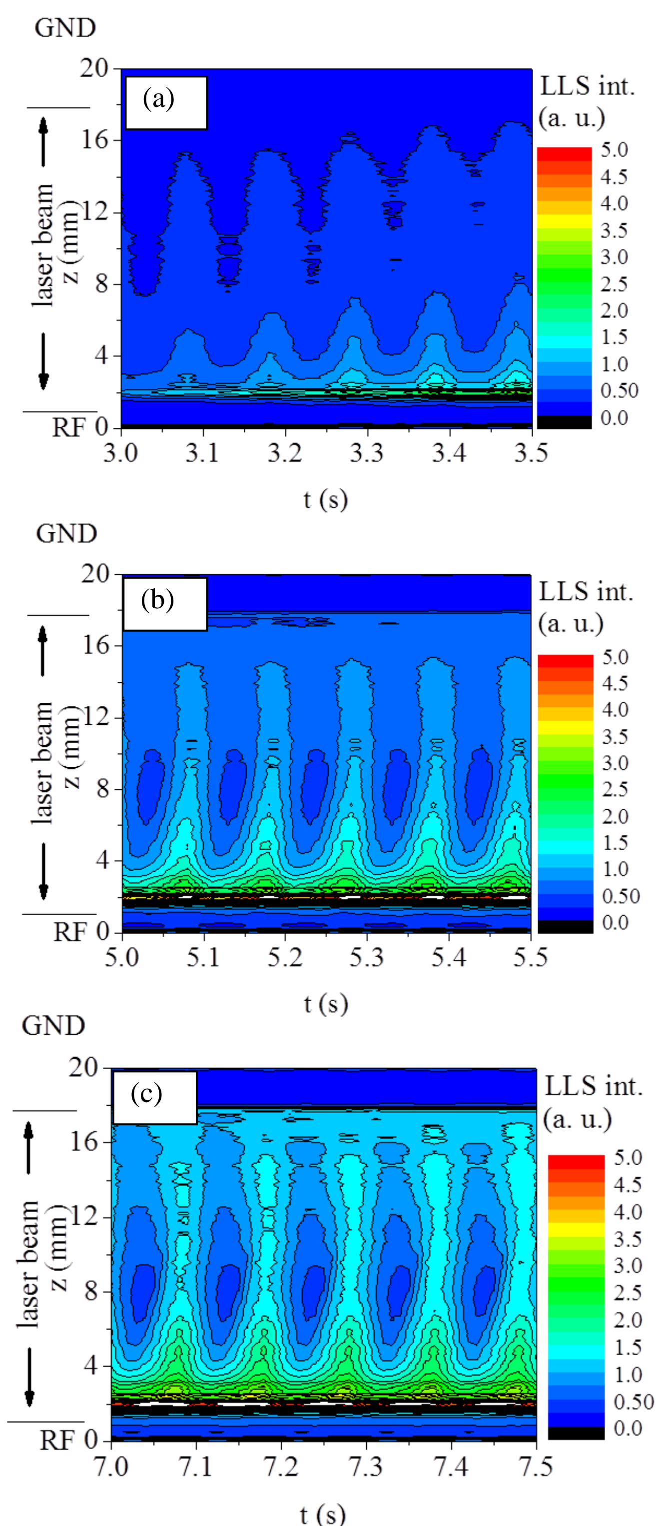

Fig. 2. Time evolution of spatial profile of nanoparticle amount for f_{AM}= 10 Hz druing (a) t = 3-3.25 s, (b) t = 5-5.25 s, and (c) t = 7-7.25 s.

have measured time evolution of spatial profile of nanoparticle amount. Here, the nanoparticle amount is defined as LLS intensity which is proportional to the density of nanoparticles and the sixth power of their size, because their size is much smaller than the wavelength of the laser light, namely, in the Rayleigh scattering regime. Figure 2 shows time evolution of spatial profile of nanoparticle amount at the center of electrode (r = 0 mm) for f_{AM}= 10 Hz. For t= 3 s, most nanoparticles are located at the plasma/sheath boundary near the powered electrode (z~2mm) where nanoparticles mainly generate and grow. Large amount region of nanoparticles is oscillated at 10 Hz. The large amount region extends when the discharge power is high during each period of AM, whereas it reduces when the discharge power is low. The oscillation of the nanoparticle amount in the plasma bulk center around z= 10 mm shows phase delay of 25° compared with those at the plasma/sheath boundaries near the powered and grounded electrode as shown in Figs. 2(b) and 2(c). The phase delay corresponds to the extension speed of 70 cm/s. For the longer time scale, the large amount region extends gradually toward the upper grounded electrode, and it reaches the plasma/sheath boundary near the upper grounded electrode around t= 7 s, which suggests that nanoparticles in the plasma grow with time.

Figure 3 shows time evolution of spatial profile of nanoparticle amount at the center of electrode for f_{AM}= 20 Hz. General behavior of nanoparticles for f_{AM}=20 Hz is similar to that for f_{AM}= 10 Hz. Nanoparticle amount and nanoparticle located area for f_{AM}= 20 Hz are much smaller than those for f_{AM}= 10 Hz. These differences between results in Figs. 2 and 3 indicate growth of nanoparticles is suppressed by increasing the AM frequency.

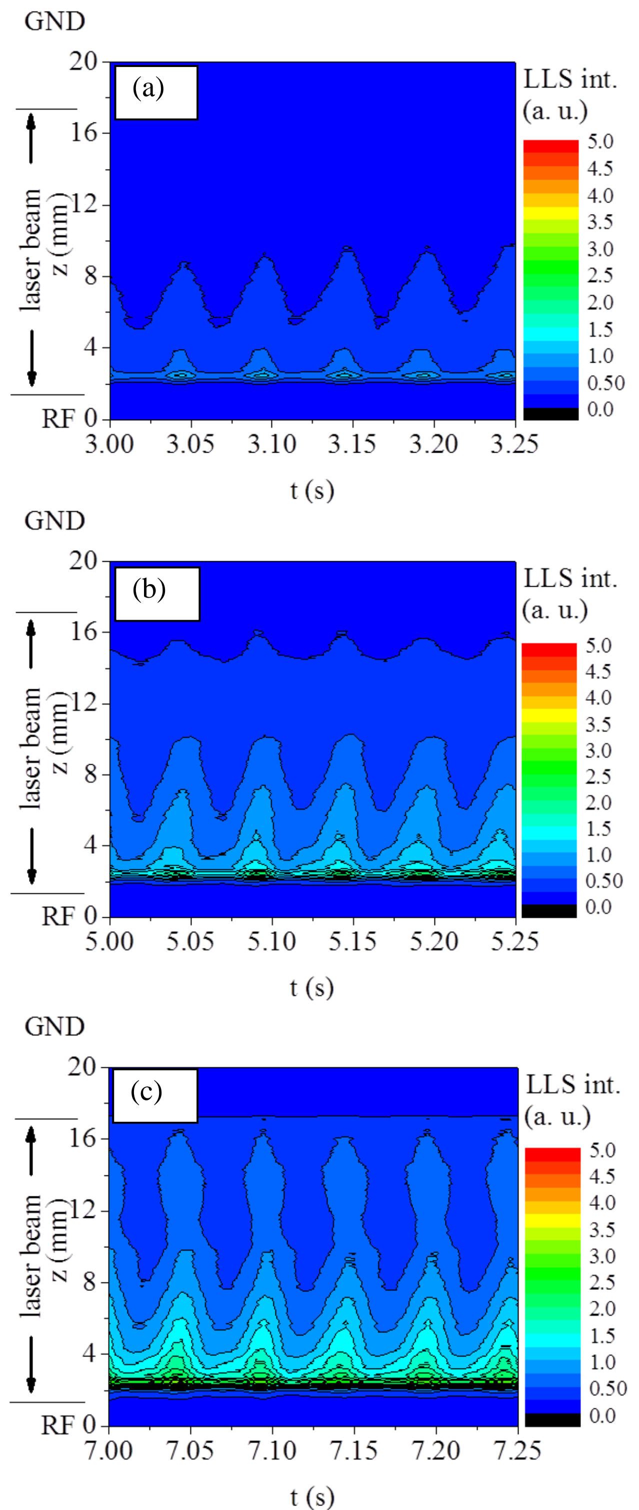

Fig. 3. Time evolution of spatial profile of nanoparticle amount for f_{AM}= 20Hz druing (a) t = 3-3.25 s, (b) t = 5-5.25 s, and (c) t = 7-7.25 s.

4. Conclusions

We have measured time evolution of spatial profile of nanoparticle amount in reactive plasmas to obtain information on effects of plasma fluctuation on the nanoparticle growth in the initial growth phase. Amplitude modulation of discharge voltage leads to oscillate nanoparticle amount and their spatial profile. Growth of nanoparticles is suppressed by increasing the AM frequency.

Further elaborate study is required to control of size, strurture, agglomeration, morphology, surface, defect, dopant, and impurity of nanoparticles. Such control will open a new era of nanoparticle technology.

5. Acknowledgment

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6. References

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