Analysis of coupling between nanoparticles and radicals using perturbation of radical density in reactive plasmas

ラジカル密度摂動によるナノ粒子とラジカルのカップリング解析

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Coupling between nanoparticles and radicals in short and long time scale was analyzed by applying perturbation of radical density in reactive plasmas. Non-linear coupling between nanoparticles and radicals is suggested by spectrum analysis of time evolution of nanoparticle amount measured by two dimensional laser light scattering method. Optical emission intensity measurements show spatial profiles of radical density in the device scale is coupled with the time evolution of nanoparticle amount.

1. Introduction

Understanding linear and non-linear interactions between plasmas and surface of nano-materials is important in fabrication of semiconductor devices and nanostructures. For instance, device performance often depends on perturbations of interactions in nanometer scale. To study such interactions, we have employed nanoparticles in reactive plasmas as a model of nano-inteface between plasmas and nanostructure and studied growth of nanoparticles with amplitude modulation (AM) to perturb radical density in the plasmas. Recently, we have revealed that applying AM suppresses growth of nanoparticles [1-5]. We have analyzed dynamics of radical density and nanoparticle amount to understand the interaction between plasmas and nanoparticles by measuring spatiotemporal profiles of particle amount and radicals. Here we report the experimental results.

2. Experimental

We employed a capacitively-coupled discharge reactor equipped with a two-dimensional laser light scattering (LLS) system as shown in Fig. 1 [4]. $Si(CH_3)_2(OCH_3)_2$ (DM-DMOS) diluted with Ar gas was supplied to the reactor as precursor molecules. The flow rate of Ar and DM-DMOS were 40 sccm and 0.2 sccm, respectively. The total gas pressure was 1.25 Torr. We applied high frequency voltage of 60 MHz for 8 seconds between the powered and grounded electrodes to generate discharges. The discharge voltage was 120 V, which corresponds to the power of 30 W. For the amplitude modulation experiments, AM frequency f_{AM} was 100 Hz and the AM level was 30 %. A sheet beam of YAG laser light (λ= 532 nm and 2 W) was irradiated between the powered electrode and the upper grounded electrode from side of the reactor. We have measured 90° Rayleigh scattering from nanoparticles using a high speed camera (Photoron FASTCAM SA4) equipped with an interference filter of 532 nm with 1 nm FWHM at a frame rate of 1000 fps. Optical emission intensities from Ar I lines of 750.4nm and 811.5nm were measured using the same camera with interference filters of a center wavelength of 750 nm and 810 nm with 10 nm FWHM.

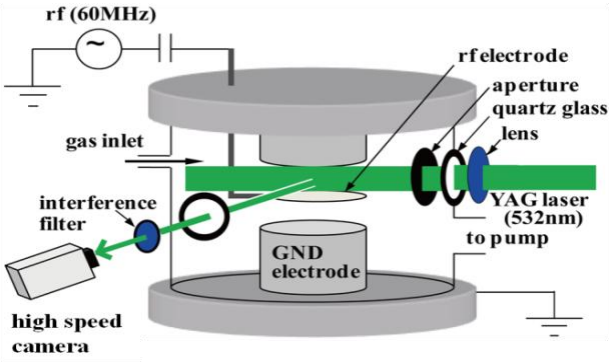

Fig. 1. Experimental setup.

3. Results and Discussion

Optical emission intensities of Ar I 750.4 nm and 811.5 nm give information of generation rate of radicals. The 750.4 nm emission takes place due to the direct excitation:

$Ar + e \rightarrow Ar(4p'[1/2]_0) + e$ ($\varepsilon \geqq 13.48$eV) ,

$Ar(4p'[1/2]_0) \rightarrow Ar(4s'[1/2]_1) + h\nu$ (750.4nm).

Ar I 811.5 nm is emitted by the two step excitation:

$Ar + e \rightarrow Ar^m(4s[3/2]_2) + e$ ($\varepsilon \geqq 11.55$eV),
$Ar^m + e \rightarrow Ar(4p[5/2]_3) + e$ ($\varepsilon \geqq 1.53$eV), and
$Ar(4p[5/2]_3) \rightarrow Ar^m(4s[3/2]_2) + h\nu$ (811.5nm).

The ratio intensity of 811.5nm to 750.4nm gives information on Ar metastable density [6-7]. We have employed the ratio as an indicator of radical density.

Figure 2(a) shows spatial profiles of power spectrum of the optical emission intensity ratio. The peaks of fluctuation of the optical emission intensity ratio are observed at the fundamental frequency and higher harmonics of f_{AM}. It indicates perturbation of radical density is directly coupled with amplitude modulation of the discharge voltage. Figure 2(b) shows that of LLS intensity which indicates particle amount. The LLS intensity is also perturbed at the fundamental frequency and higher harmonics of f_{AM}. In addition, perturbation at sub-harmonics such as $f = 3/5f_{AM} = 60$Hz are observed in Fig. 2(b). It suggests that the amount of nanoparticle is non-linearly coupled with the radical density in the short time scale.

We also studied such coupling from a longer time scale. Figure 3(a) shows time evolution of ratio of 811.5nm emission intensity to 750.4 nm one at the center of the discharges. The solid squares shows results for discharges without nanoparticles (pure Ar discharges), and the solid circles shows those for discharges with nanoparticles. For the discharges without nanoparticles, the intensity ratio rapidly increases just after discharge initiation, and keeps almost constant value. For the discharge with nanoparticles, the intensity ratio is almost zero from

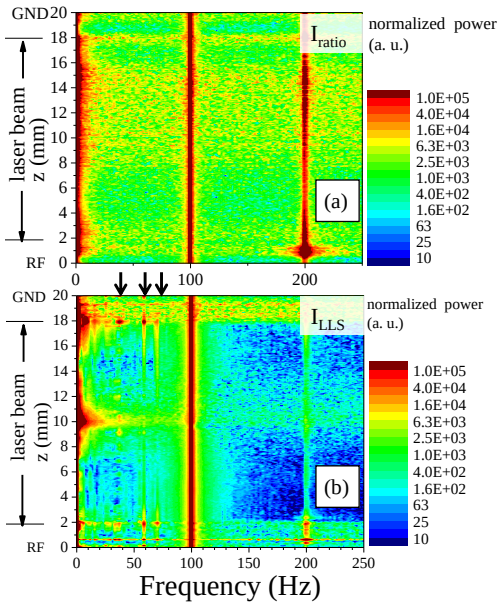

Fig. 2. Spatial profile of power spectrum of (a) optical emission intensity ratio and (b) LLS intensity.

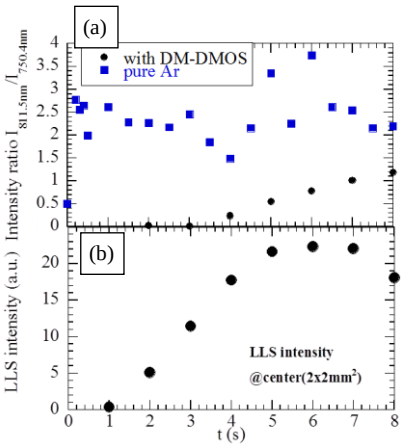

Fig. 3. Time evolution of (a) optical emission intensity ratio and (b) LLS intensity.

t= 0 s to t= 3 s then increases gradually with t. Figure 3(b) shows time evolution of the LLS intensity I_{LLS} at the center of the discharges. The I_{LLS} monotonically increases with increasing t from t = 1 s, then is saturated around t= 5 s. The characteristic rise time of LLS intensity is almost the same as that of the emission intensity ratio. This long time scale coupling is caused by the fact that the rather slow growth of nanorpaticles modifies radical density.

4. Conclusion

We have measured the ratio of optical emission intensities of 811.5nm to 750.4nm and LLS intensity. The optical emission ratio hows the perturbation of radical density by amplitude modulation of discharge voltage. The characteristic time of increase of the ratio is similar to that of the amount of nanoparticles. There are two kinds of coupling: the short time scale of several ms is caused by the fact that perturbation of radical density modify the nanoparticle growth, and the long time scale coupling is caused by the fact that the rather slow growth of nanorpaticles modifies radical density.

Acknowledgments

This work was partly supported by JSPS KAKENHI grant number 26246036.

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