Detection of Nano-particles Formed in CVD Plasmas using a Two-Dimensional Photon-Counting Laser-Light-Scattering Method

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To detect nano-particles formed in CVD plasmas, we have developed a high sensitivity two-dimensional photon-counting laser-light-scattering (2DPCLLS) method. Size and density of nano-particles are determined from their thermal coagulation that takes place after turning off discharges. The 2DPCLLS system realizes detection of nano-particles from 1.3 nm in size and 10^{12} cm^{-3} in number density to 6 nm and 10^{8} cm^{-3}. It provides easy observation of their transport with a high time resolution of 33 μs and a good spatial resolution of 1x1.25x1.25 mm^3.

Keywords: laser-light-scattering method, nano-particle, CVD plasma, transport, thermal coagulation

1. Introduction

Nano-particles are often formed in processing discharge plasmas [1-5]. They may contaminate etching and deposition processes in the top-down approach [1-5], whereas they can be employed as nano-blocks in the bottom-up approach [6, 7]. For instance, to realize mass-production of a-Si:H solar cells of high stability against light soaking, reduction of incorporating amorphous Si nano-particles of 1-10 nm in size into a-Si:H films is needed because such incorporation tends to degrade stability of the films [8-10].

Laser-light-scattering (LLS) methods have been frequently applied to detect nano-particles formed in processing discharge plasmas [1-6, 11-18]. Because nano-particles less than 5 nm in size are hard to be detected using the conventional one or two dimensional LLS methods, little information about their transport and sticking probability on films are available. We have proposed a high sensitivity photon-counting laser-light-scattering method to detect such nano-particles down to 1 nm in size formed in CVD plasmas [14]. Recently, based on the method we have developed a two-dimensional photon-counting laser-light scattering (2DLLS) method to obtain information about the transport of nano-particles of 1-10 nm in size. In this paper, we describe the 2DLLS method together with the experimental results obtained by the method.

2. Experimental

Experiments were carried out using a capacitively coupled rf discharge reactor described elsewhere as shown in Fig. 1 [16, 1]. Nano-particles were formed in 13.56 MHz rf discharges of $Si(CH_3)_2(OCH_3)_2$ diluted with Ar. To dissociate $Si(CH_3)_2(OCH_3)_2$ and form nano-particles, we generated a plasma by applying 728 peak-to-peak voltage of 13.56 MHz to the powered electrode for a discharging period T_{on} =0.08-4.0 s as shown in Fig. 2. The mean size of nano-particles can be controlled by the discharging period T_{on} [6]. The corresponding discharge power was 75 W.

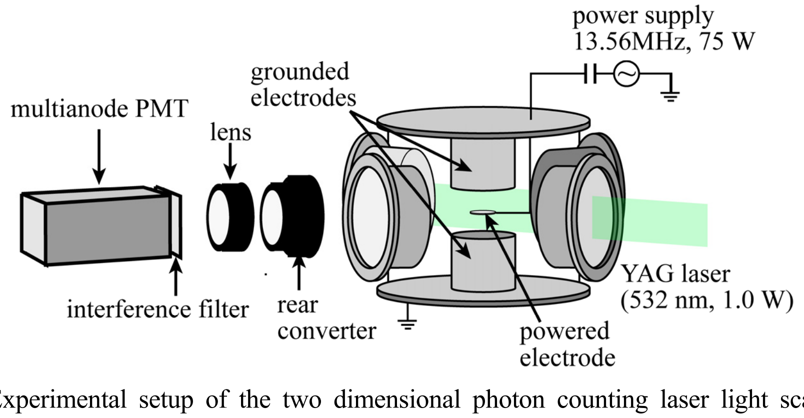

Fig. 1. Experimental setup of the two dimensional photon counting laser light scattering (2DLLS) system together with the reactor.

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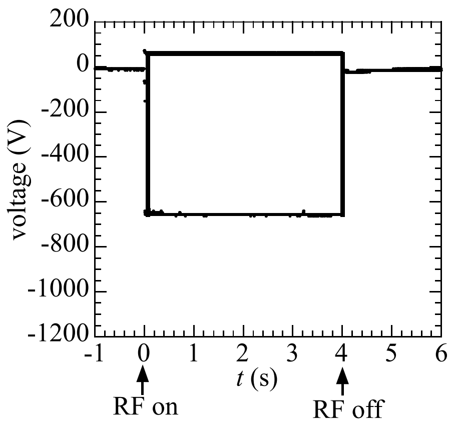

Fig. 2. Envelope of the discharge voltage. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =4.0 s, 75 W, T_s =373 K.

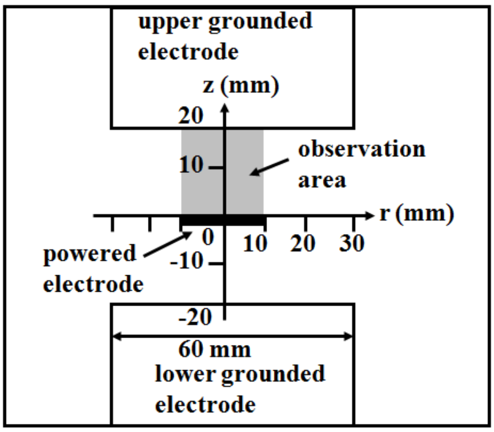

Fig. 3. Cross-sectional view of reactor and observation area of 2DPCLLS measurements with the multianode PMT.

Spatiotemporal evolution of size and density of nano-particles was measured in a region as shown in Fig. 3, using a 2DLLS method [18] combined with a simple method for deducing their size and density [14]. For the 2DPCLLS method, a sheet beam of YAG laser light of 1.0 W at 532 nm was passed parallel to the surface of the upper grounded electrode. The height and width of the sheet beam was 20 mm and 1 mm, respectively. The intensity of light scattered by nano-particles was detected at right angles with a multianode PMT (Hamamatsu H9500) equipped with an interference filter of a center wavelength of 532 nm and FWHM of 1 nm. The PMT has 16x16 multianode, that is, 256 pixels. The output signal of each pixel was simultaneously obtained with a multichannel scaler of a channel gate width from 33 μs to 10 ms. The total absolute sensitivity of the measurement system was calibrated using Rayleigh scattering of N_2 gas.

The size (diameter) and density of nano-particles were deduced from their thermal coagulation that took place after turning off the discharges [14]. When time evolution of the light intensity scattered by nano-particles is

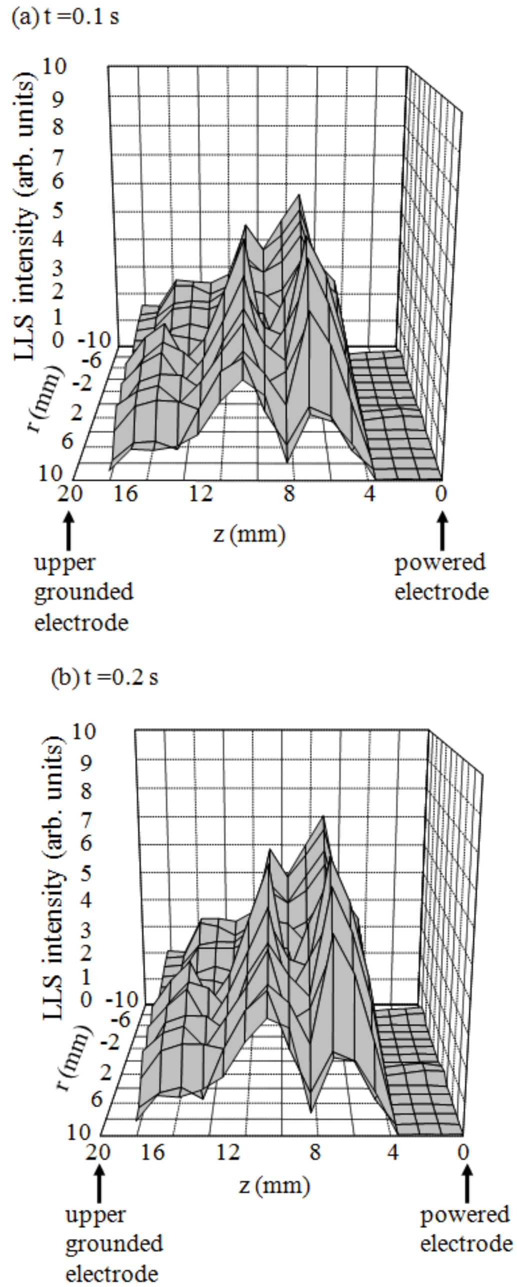

Fig. 4. LLS intensity profiles for t =0.1 s (a) and t =0.2 s (b). Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =4.0 s, 75 W, T_s =329 K.

determined by that of their size and density varied mainly due to the their thermal coagulation, the intensity I in the Rayleigh scattering regime is given by,

$$I(t) = \frac{B}{n_{p0}} + Bkt \qquad (1)$$

where n_{p0} is the density of nano-particles before initiation of the coagulation, k is the coagulation coefficient, and B is a constant which relates to polarizability of nano-particles and sensitivity of the optical detection system. Hence, we can deduce nano-particle density by fitting eq. (1) to the observed time evolution of the LLS intensity after turning off discharges. Nano-particle size is obtained using the density and absolute LLS intensity. The full description of the analysis method taking transport of nano-particles into account was reported elsewhere [14]. Two dimensional data offers clear information both on transport of nano-particles and on their growth.

3. Results and discussion

Figure 4 shows LLS intensity profiles for (a) t = 0.1 s after turning on the discharge and (b) t = 0.2 s. During the discharging period, nano-particles are generated mainly in the plasma/sheath boundary region between z =10 and 14 mm near the powered electrode. A large number of them reside in their generation region resulting from the balance between ion drag force which pushes nano-particles towards the powered electrode and electrostatic force which repels them towards plasma bulk [2, 4].

Figure 5 shows time evolution of diameter and density of nano-particles during discharging period T_{on}. With increasing t from 0.08 s to 4.0 s, their diameter increases from 1.3 nm to 26 nm, whereas their density decreases from $8x10^{11}$ cm^{-3} to $1.5x10^{9}$ cm^{-3}. Nano-particles grow with time predominantly via accretion of neutral radicals from the gas phase during the discharges [6]. Using the new 2DPCLLS system nano-particles down to 1.3 nm in size can be detected, whereas using our previous LLS system [18] in which ICCD camera is employed, it is hard to detect nano-particles less than 5 nm in size because the sensitivity of ICCD camera is much lower than that of the multianode PMT. Time and spatial resolution of the new LLS system are 33 μs and $1x1.25x1.25$ mm^3, which corresponds to the laser sheet width and one pixel of 16x16 pixels for the observation area of -10 mm $\leq r \leq$ 10 mm and $0 \leq z \leq 20$ mm, while those of the previous LLS system are 33 ms and $1x0.028x0.042$ mm^3, which corresponds to the laser sheet width and one pixel of 720x480 pixels for the observation area of 0 mm $\leq r \leq$ 20 mm and $0 \leq z \leq 20$ mm. Therefore, the 2DPCLLS system is a promising one for detecting nano-particles less than 5 nm in size with a high time resolution and a good spatial resolution.

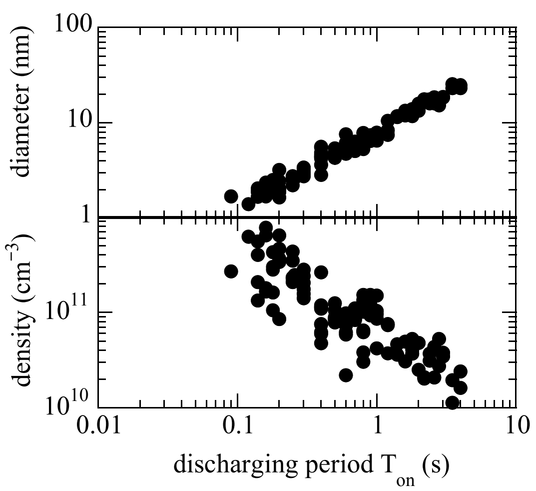

Fig. 5. Time evolution of diameter and density of nano-particles during discharging period T_{on}. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =0.08-4.0 s, 75 W, T_s =368 K.

Figure 6 shows time evolution of LLS intensity as a parameter of z. When the density of nano-particles is higher than a critical density for their coagulation [14], they begin to coagulate just after turning off discharges. Their density decreases rapidly due to the coagulation (coagulation dominant period), and hence the coagulation nearly ends in a short period because the coagulation rate is proportional to the square of their density. After the coagulation dominant period, nano-particles are transported towards the upper grounded electrode (transport dominant period). The durations of these periods depend on z. At z = 2 mm in Fig. 6, for instance, the time evolution of the LLS intensity is determined mainly by coagulation of nano-particles for t = 2.0-2.1 s and then by their transport for t ≥ 2.15 s. From the results in the transport dominant period in Fig. 6 the trajectory of nano-particles is obtained as shown in Fig. 7. After turning off discharges, nano-particles are transported from their generation region near the powered electrode towards the upper grounded electrode at a velocity about 2.1 cm/s by thermophoretic force due to the temperature gradient of 7 K/cm from the powered electrode to the upper grounded electrode [13, 16, 17]. Therefore, the 2DPCLLS system is a promising one for observation of the transport of nano-particles.

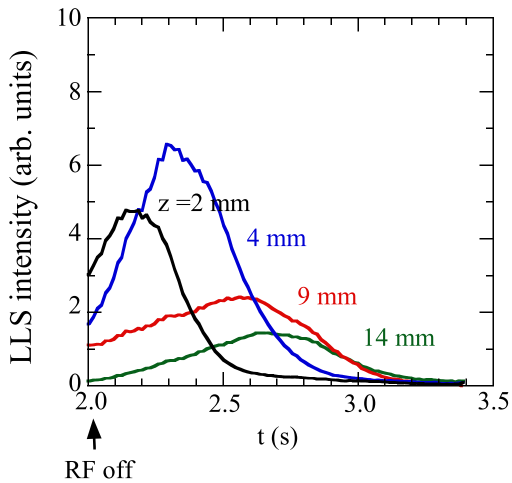

Fig. 6. Time evolution of LLS intensity as a parmeter of z. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =2.0 s, 75 W, T_s =329 K.

Figure 8 shows the detection limit of the 2DPCLLS system with the multianode PMT and the previous 2DLLS system with the ICCD camera. The detection limit of 2DPCLLS system has been significantly improved compared with the 2DLLS system. The 2DPCLLS system realizes detection of nano-particles from 1.3 nm in size and 10^{12} cm^{-3} in number density to 6 nm and 10^{8} cm^{-3}. This detection limit is sufficient to detect amorphous Si nano-particles of 1-10 nm in size which tend to degrade the stability of a-Si:H films against light soaking [10].

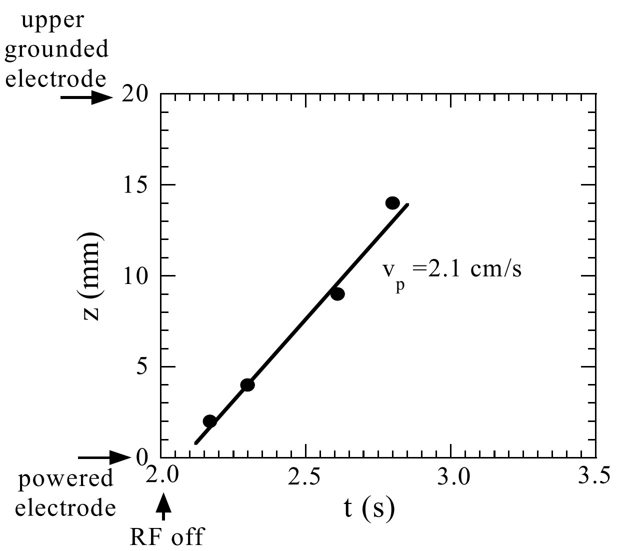

Fig. 7. Trajectory of nano-particles after turning off discharges. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =2.0 s, 75 W, T_s =329 K.

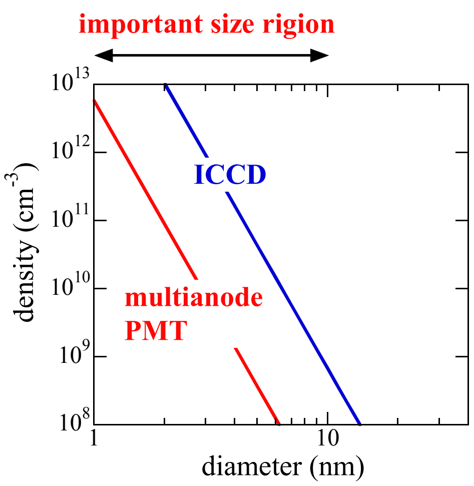

Fig. 8. Detection limit of 2DPCLLS system with multianode PMT and that of previous 2DLLS system with ICCD camera.

4. Conclusions

We have developed the high sensitivity 2DPCLLS method. Size and density of nano-particles are determined from their thermal coagulation that takes place after turning off discharges. The 2DPCLLS system provides detection of nano-particles from 1.3 nm in size and 10^{12} cm^{-3} in number density to 6 nm and 10^{8} cm^{-3}. It provides easy observation of their transport with a high time resolution of 33 μs and a good spatial resolution of 1x1.25x1.25 mm^3.

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