Control of Three Dimensional Transport of Nano-blocks by Amplitude Modulated Pulse RF Discharges using an Electrode with Needles

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We have proposed a bottom-up nanosystem-fabrication method, which consists of production of nano-blocks and radicals (adhesives) in reactive plasmas, transport of nano-blocks towards a substrate, their arrangement on the substrate using pulse RF discharges with the amplitude modulation (AM) of discharge voltage. In this study, we report transport of nano-blocks by AM discharges using an electrode with needles. During the modulation period, nano-blocks are transported from their generation region near the powered electrode towards a needle of the electrode at a velocity of 9.8 cm/s due to ion drag force towards the needle, indicating that the method utilizing the pulse RF discharges with AM is a promising one for control of nano-block transport in three dimensions.

Keywords: nano-block manipulation, transport, amplitude modulation, pulse RF discharge, nanosystem

1. Introduction

Recent progress in nano-materials has made them attractive for an increasing number of their applications, for instance, electronics, medical components, fillers, catalysts, and fuel cells [1-8]. Nano-materials need structures and components which exhibit novel and significantly improved physical, chemical and biological properties, because of their nanoscale size, and hence fabrication of nano-materials by bottom-up methods as well as that by top-down ones are required. Several examples of the bottom-up methods are as follows. A. Heeren, et al. realized micro- and nano-block manipulation in fluids for biological applications [9], J. W. G. Wildoer, et al. showed transistorlike behavior in carbon nanotubes [10], and V. Balzani, et al. reported the structural and functional design of molecular devices [11]. A wide variety of nano-material and nano-system fabrication methods are required to be developed to realize complex nano-world.

We have proposed a novel bottom-up method for nano-material and nanosystem fabrication [12-14]. Our method consists of production of nano-blocks and radicals (adhesives) in reactive plasmas, their transport towards a substrate, arrangement of nano-blocks on the substrate using pulse radio frequency (RF) discharges with the amplitude modulation (AM) of discharge voltage. For the method, the control of the size of nano-blocks and the accurate manipulation of nano-blocks without their agglomeration are important.

Up to now, we have succeeded in controlling the size of nano-blocks by pulse RF discharges [15, 16], and have realized their rapid transport from their generation region towards a substrate by pulse RF discharges with AM [12-14]. Therefore, the method utilizing the pulse RF discharges with AM is a promising one to realize one dimensional transport of nano-blocks. On the basis of the results, we have observed the transport of nano-blocks by AM discharges using an electrode with needles to realize three dimensional transport control of nano-blocks. In this paper, we describe the experimental results and discuss the transport of nano-blocks by AM discharges using the electrode with needles.

2. Experimental

Experiments were carried out using a capacitively coupled RF discharge reactor as shown in Fig. 1 [12-14]. A powered disc electrode of 10 mm in diameter and 1 mm in thickness was set in the middle of two grounded electrodes of 60 mm in diameter placed at a distance of 40 mm, in the reactor of 260 mm in inner diameter and 230 mm in height. Two needles of 5 and 10 mm in length were set on the upper grounded electrode as shown in

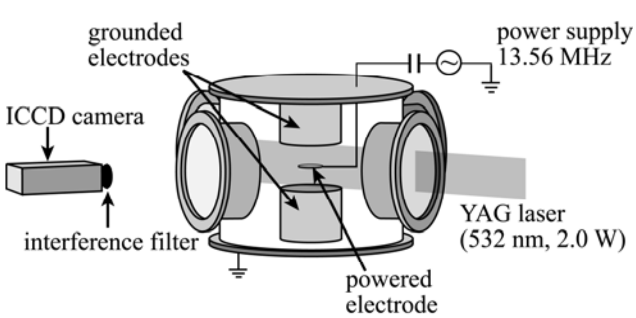

Fig. 1. Experimental setup of the two-dimensional laser light-scattering system (2DLLS) together with the reactor.

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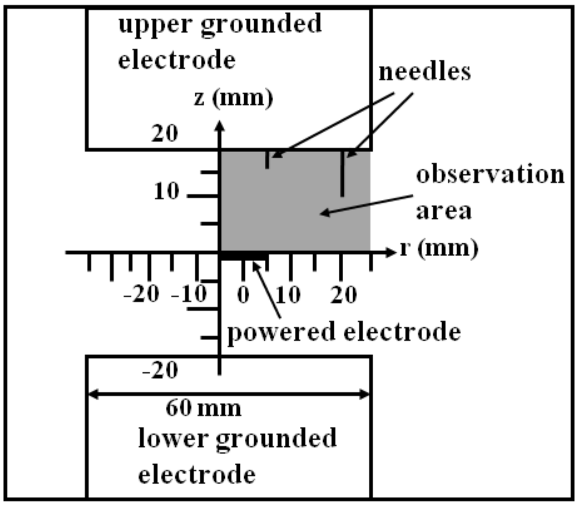

Fig. 2. Cross-sectional view of reactor and observation area of 2DLLS measurements with the ICCD camera.

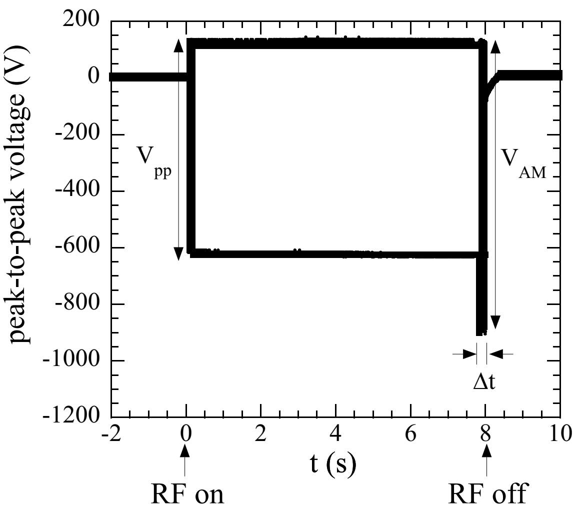

Fig. 3. Envelope of the discharge voltage. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =8.0 s, Δt =200 ms, V_{AM} = 1020 V, 60 W, T_s =343 K.

Fig. 2. Nano-blocks 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-blocks, we generated a plasma by applying 741 peak-to-peak voltage of 13.56 MHz to the powered electrode for a discharging period T_{on} = 8.0 s as shown in Fig. 3. The self-bias voltage was -250 V. The mean size of nano-blocks can be controlled by the discharging period T_{on} [15, 16]. The corresponding discharge power was 60 W. For AM discharges, the discharge voltage was modulated as shown in Fig. 3. The peak-to-peak voltage V_{AM} during the modulation and the modulation period Δt were set to be 1022 V and 200 ms, respectively. The self-bias voltage during the modulation period was -390 V.

Spatiotemporal evolution of size and density of nano-blocks was obtained in a region as shown in Fig. 2, using a two-dimensional laser-light-scattering (2DLLS) method [17] combined with a simple method for deducing their size and density [15]. For the 2DLLS method, a sheet beam of YAG laser light of 2.0 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-blocks was detected at right angles with an ICCD camera (Hamamatsu C4077-04) equipped with an interference filter of a center wavelength of 532 nm and FWHM of 1 nm. Time and spatial resolution of the ICCD camera are 33 ms and 1x0.042x0.042 mm^3, which corresponds to the laser sheet width and one pixel of 720x480 pixels for the observation area of -5 mm $\leq r \leq$ 25 mm and $0 \leq z \leq 20$ mm. The total absolute sensitivity of the measurement system was calibrated using Rayleigh scattering of N_2 gas.

The size (diameter) and density of nano-blocks were deduced from their thermal coagulation that took place after turning off the discharges [15]. Two dimensional data offers clear information both on transport of nano-blocks and on their growth.

3. Results and discussion

Figures 4 (a) shows two-dimensional spatial images of LLS intensity as a parameter of time t. During the discharging period, nano-blocks are mainly generated in the plasma/sheath boundary region near the powered electrode, and a large number of nano-blocks reside in their generation region resulting from the balance between ion drag force which pushes nano-blocks towards the powered electrode and electrostatic force which repels them towards plasma bulk [12, 13]. Nano-blocks become larger with time mainly via CVD on their surface. Just after turning off the discharges, the size of nano-blocks and their number density are about 44 nm and 8.2×10^9 cm^{-3}, respectively [15].

After turning off unmodulated discharges, nano-blocks move away from their generation region around the powered electrode towards the upper grounded electrode. In the z-direction nano-blocks move at a velocity of 2.5 cm/s for t = 8.0-8.4 s. It should be noted that needles have little effects on the transport. After turning off the discharge, transport of nano-blocks is determined by the balance between thermophoretic force and gas viscous force [12, 13]. Their velocity v_d is given by

$$v_d = \frac{3p\lambda \nabla T}{\pi n_g m_g v_g T}, \qquad (1)$$

where n_g is the number density of gas molecules, m_g and v_g their mass and thermal velocity, p the gas pressure, λ the mean free path of gas molecules, and T and ∇T the gas temperature and its gradient. The experimental results described elsewhere [12, 13] shows the velocity of nano-blocks can be well expressed by Eq. (1).

During the modulation period in Fig. 4 (b), nano-blocks are transported at a velocity of 9.8 cm/s from their generation region around the powered electrode towards the upper grounded electrode. Figure 5 shows two-dimensional spatial profiles of the LLS intensity during the modulation period. Just after the beginning of turning on the modulation (t = 7.8 s), nano-blocks reside around the powered electrode, and then they are transported at a velocity of 9.8 cm/s towards the long needle. We also found that longer Δt and larger V_{AM} needed to drive larger nano-blocks due to their large inertia. Thus, two key parameters for driving nano-blocks are the discharge voltage and the period of the modulation.

Figure 6 (a) shows the spatial profiles of optical emission intensity in the z-direction at r = 0 mm. At the beginning of the modulation, the width of the optical sheath near the powered electrode increases from 3.2 mm to 3.4 mm. A time averaged plasma potential is expressed as

$$<V_p> = \left(\frac{\omega}{2\pi}\right)\left(\frac{kT_e}{e}\right)\int_0^{\frac{2\pi}{\omega}} dt \ln\left[\frac{1+\frac{A_c}{A_a}\exp\frac{eV(t)}{kT_e}}{1+\frac{A_c}{A_a}}\right]$$

$$+\left(\frac{kT_e}{2e}\right)\ln\left(\frac{m_i}{2.3m_e}\right), \qquad (2)$$

where k, T_e, and e is Boltzman's constant, the electron temperature and the electronic charge, respectively [18, 19]. A_c and A_a are the cathode area and the anode one, and m_i and m_e are the mass of the ions and electrons. The applied RF voltage $V(t)$ with its frequency ω is given by

$$V(t) = V_{RF}\sin\omega t + V_{DC}, \qquad (3)$$

where V_{RF} and V_{DC} are the RF voltage and the negative self-bias, respectively. A_c and A_a are expressed as

$$\left(\frac{A_a}{A_c}\right)^{\frac{\pi}{2}} \approx \frac{V_{RF}+V_{DC}}{V_{RF}-V_{DC}}, \qquad (4)$$

The potential in the sheath may be expressed as

$$\phi = -\frac{en_s}{\varepsilon_0}x^2, \qquad (5)$$

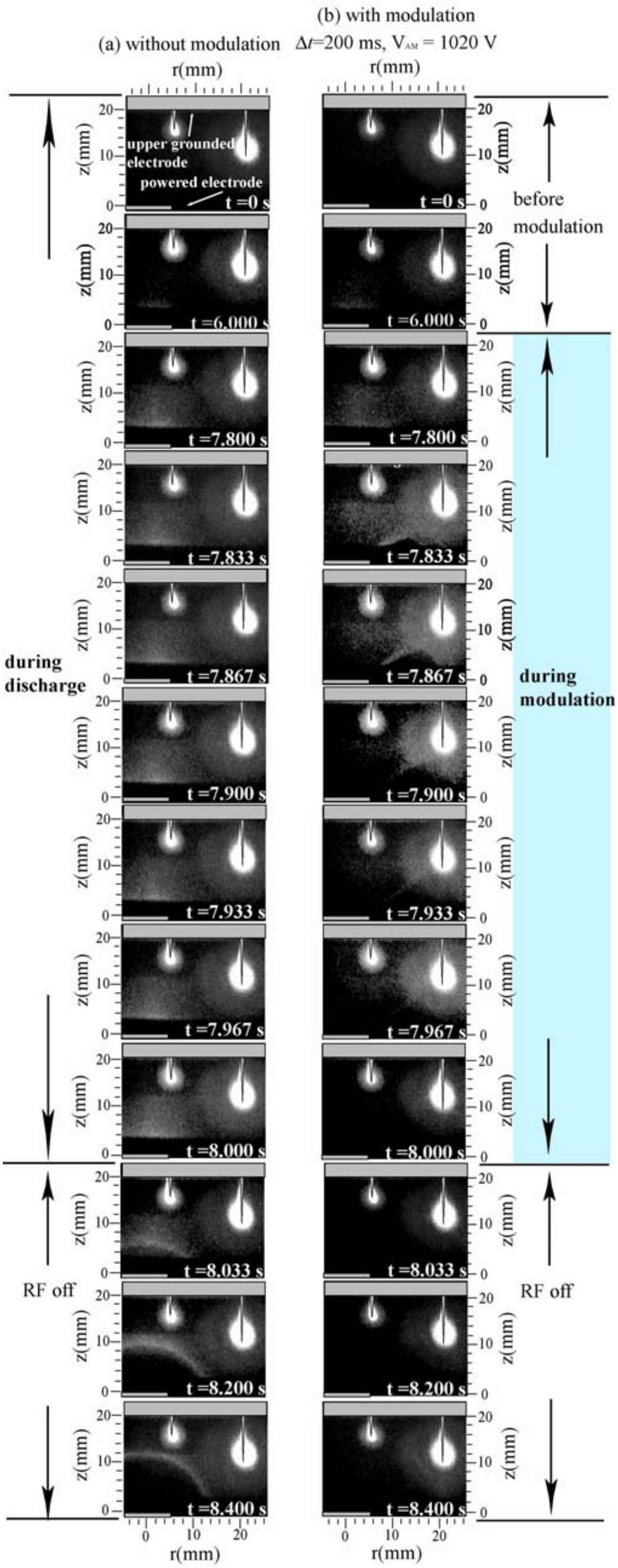

Fig. 4. Two-dimensional spatial images of LLS intensity as a parameter of time t without (a) and with (b) AM. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =8.0 s, 60 W, T_s =343 K.

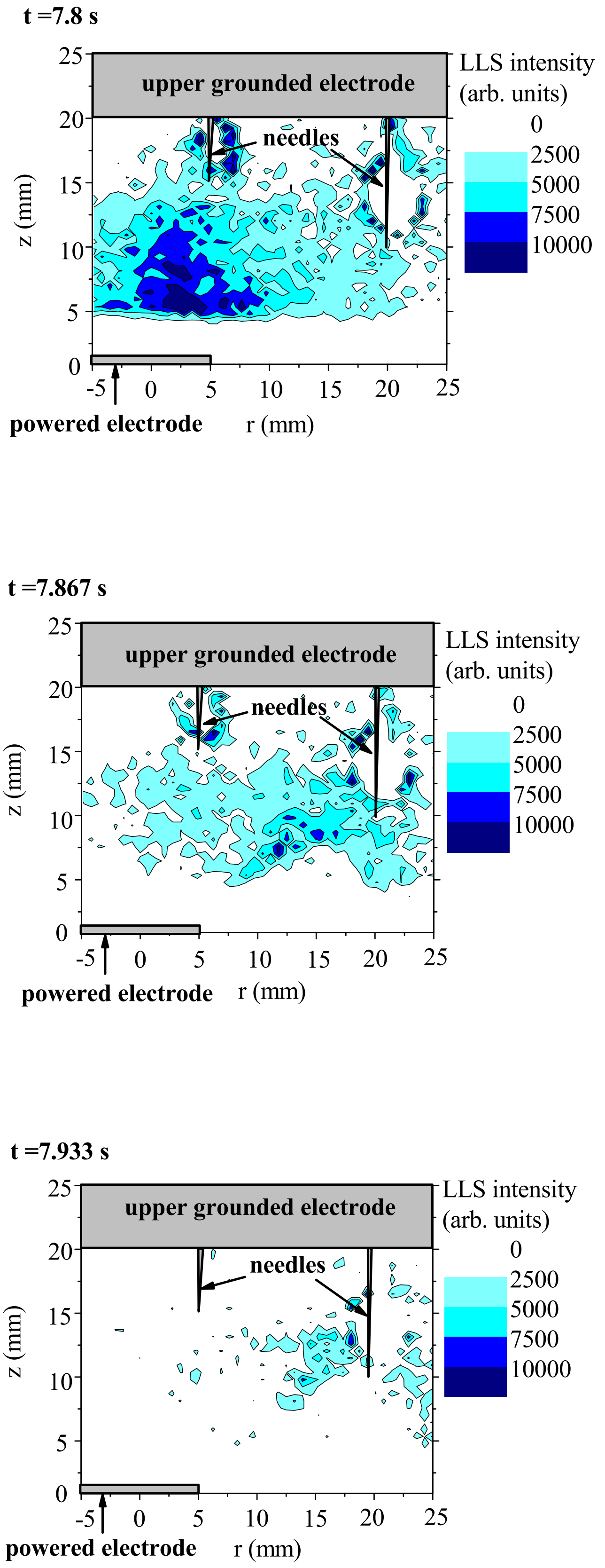

Fig. 5. Two-dimensional spatial profiles of LLS intensity during the modulation period. Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =8.0 s, Δt =200 ms, V_{AM} = 1020 V, 60 W, T_s =343 K.

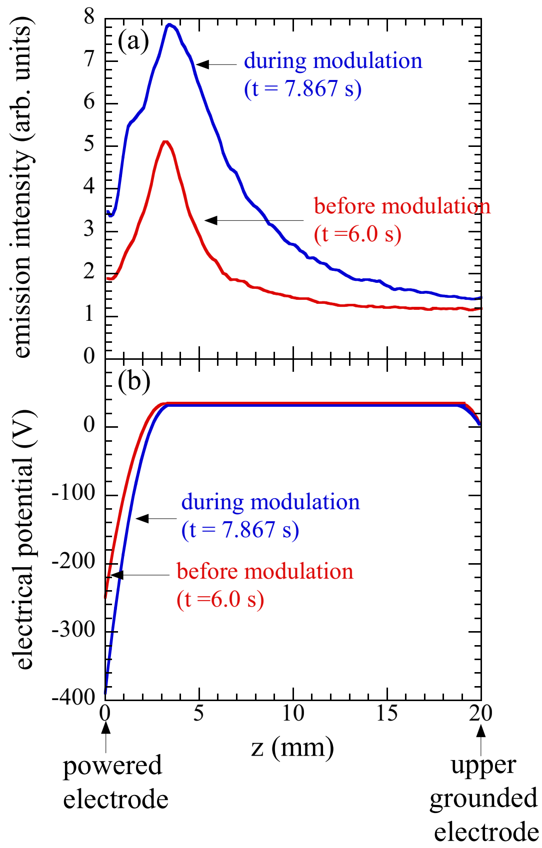

Fig. 6 . Spatial profiles of optical emission intensity (a) and time averaged electrical potentials before and during modulation (b). Ar 40 sccm, $Si(CH_3)_2(OCH_3)_2$ 0.2 sccm, 1.0 Torr, T_{on} =8.0 s, Δt =200 ms, V_{AM} = 1020 V, 60 W, T_s =343 K.

where, ϕ, n_s, ε_0, and x are the electrical potential, plasma density at the sheath edge, vacuum permittivity, and the distance between the wall to the sheath edge. From Eqs. (2)-(5), electrical potentials before and during modulation are obtained as shown in Fig. 6 (b) using kT_e/e = 3 V and m_i = 40, which is the mass of Ar^+.

Because of their large inertia, just after the modulation nano-blocks charged negatively tend to remain in the sheath and electrostatic force drives them towards plasma bulk. Then they are transported towards the long needle due to ion drag force towards the needle. Such transport during the modulation period requires an asymmetric potential as shown in Fig. 6 (b), in other words, a large voltage drop across the sheath near the powered electrode [13]. Therefore, the method employing the pulse RF discharges with AM is a promising method for control of three dimensional transport of nano-blocks.

4. Conclusions

We have realized transport of nano-blocks by using AM discharges with the electrode with needles. During the modulation period, nano-blocks are transported from their generation region near the powered electrode towards the needle at a velocity of 9.8 cm/s due to ion drag force towards the needle. The method utilizing the pulse RF discharges with AM is a promising one for control of nano-block transport in three dimensions.

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