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Transport of Nano-particles in Amplitude Modulated RF Discharges

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Transport of nano-particles in amplitude modulated (AM) RF discharges has been investigated using two-dimensional laser-light-scattering (2DLLS) method. By using the modulation, nano-particles can be transported rapidly, at a velocity more than 60 cm/s, from their generation region towards the upper grounded electrode during the modulation period. Two key parameters for the rapid transport are the discharge voltage V_{AM} and the period Δt of the modulation. The rapid transport is realized for Δt longer than a threshold Δt value and V_{AM} larger than a threshold V_{AM} value. The threshold Δt value increases with the discharging period T_{on}, that is the size of nano-particles.
Key words: nano-particle, transport, RF discharge, amplitude modulation

1. INTRODUCTION

The continuing evolution of microelectronics requires the timely development of porous low dielectric constant (low-*k*) materials to improve signal propagation speed in ULSI [1, 2]. The dielectric constant ε_r of low-*k* materials is expected to be $\varepsilon_r \leq 2.0$ by the year 2012 according to the 2005 international technology roadmap for semiconductors [3]. The mechanical strength of low-*k* materials of $\varepsilon_r \leq 2.0$ deposited using conventional methods is insufficient for the requirement of on-chip wiring [4]. To deposit porous low-*k* materials having high mechanical strength, we have proposed a novel method for synthesizing ultra low-*k* porous materials ($\varepsilon_r \leq 2.0$) composed of nano-particles [5]. For the method, nano-particles as nano-building blocks and radicals as adhesives are produced in reactive plasmas, and then nano-particles are co-deposited on substrates together with radicals. Therefore, control of their size as well as transport from their generation region to substrates is important.

Up to now, we have succeeded in controlling their size using pulsed discharges [5, 6]. To obtain information about their transport, we have observed their transport in pulsed RF discharges without and with an AM of the discharge voltage using 2DLLS. In this paper, we describe the result and discuss the transport.

2. EXPERIMENTAL

Nano-particles were formed during a capacitively coupled 13.56 MHz RF discharge of $Si(CH_3)_2(OCH_3)_2$ diluted with Ar, because $Si(CH_3)_2(OCH_3)_2$ was employed as a precursor of interlayer low-*k* materials in ULSI in the microelectronics industry.

Our experimental setup is shown in Fig. 1. The stainless steel vacuum vessel of 260 mm in diameter and 230 mm in height was electrically grounded. A powered electrode with 20 mm in diameter and 1 mm in thickness was placed in the middle of two electrically grounded cylindrical electrodes with 60 mm in diameter. The gap between these two grounded electrodes was 40 mm.

$Si(CH_3)_2(OCH_3)_2$ was vaporized at 373 K and supplied to the chamber with Ar. The total gas pressure was 133 Pa by regulating the flow rates at 40 and 0.2 sccm for Ar and $Si(CH_3)_2(OCH_3)_2$, respectively.

To dissociate $Si(CH_3)_2(OCH_3)_2$ and form nano-particles, we generated a plasma by applying a peak-to-peak voltage of 816 V to the powered electrode through a matching network. For this discharge condition, the RF input power was 75 W, and the self-bias voltage was -350 V. In order to control the size of nano-particles, the discharging period T_{on} was set in a range of 2.0 to 9.0 s. For an AM discharge, the discharge voltage was modulated as shown in Fig. 2. The peak-to-peak voltage V_{AM} during the modulation was set in a range of 976 to 1193 V. The modulation period Δt was set in a range of 5 to 100 ms.

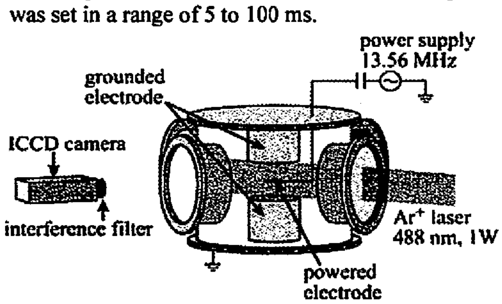

Fig. 1. Schematic view of experimental setup.

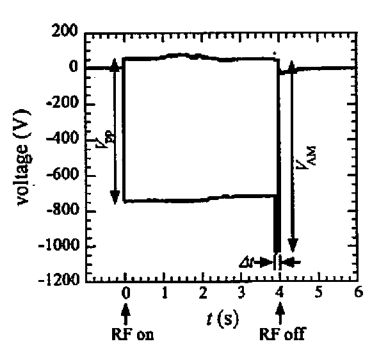

Fig. 2. Envelope of discharge voltage.

Spatiotemporal evolution of size and density of nano-particles was measured using a 2DLLS method [7] combined with a simple method for deducing their size and density [6]. For the method, a sheet beam of Ar^+ laser light of 1.0 W at 488 nm was passed parallel to the surface of the upper grounded electrode. The height and width of the sheet beam was 34 mm and 1 mm, respectively.

We detected the scattered light from nano-particles at 90 ° using an ICCD camera equipped with an interference filter of a center wavelength of 488 nm, and FWHM of 1 nm. Because the mass of nano-particles was so light ($<5\times10^{-20}$ kg) that gravity had little effect on their transport, LLS intensity in a region of $0\leq r\leq38$ mm and $0\leq z\leq20$ mm (shaded area in Fig. 3.) was employed in this study, where z =0 mm was the upper surface of the powered electrode. The size and density of nano-particles were determined from their thermal coagulation that took place after turning off discharges [6]. The deduced size agreed fairly well with those obtained by SEM and TEM observation.

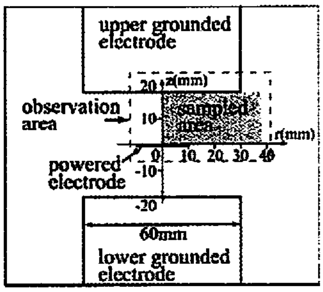

Fig. 3. Cross-sectional view of reactor and observation area of 2DLLS measurements.

3. RESULTS AND DISCUSSION

Figures 4(a) shows two-dimensional spatial images of LLS intensity as a parameter of time *t*. These images were obtained for a discharge having T_{on} =4.0 s. During the discharging period, nano-particles are mainly generated in the plasma/sheath boundary region near the powered electrode, and a large number of nano-particles reside in their generation region resulting from the

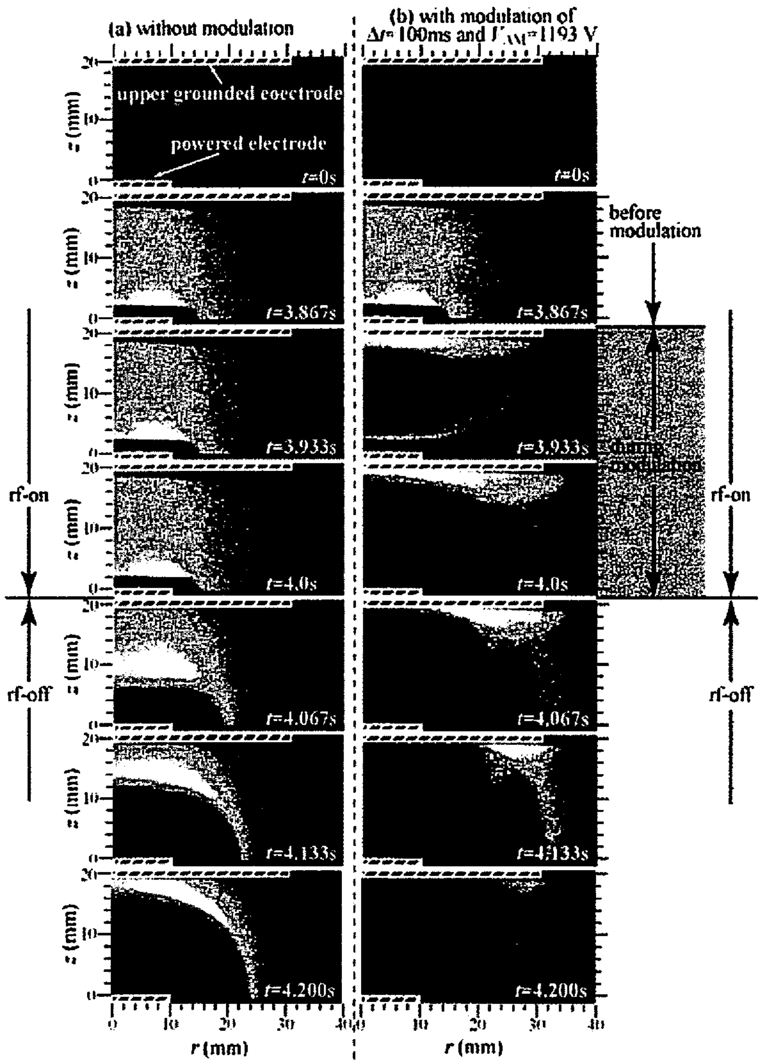

Fig. 4. Two-dimensional spatial images of LLS intensity.

balance between ion drag force which pushes nano-particles towards powered electrode and electrostatic force which repels them towards plasma bulk. Nano-particles become larger with time via their coagulation [5].

To check the shape and size of nano-particles, we carried out ex-situ TEM observation. Figure 5 shows a TEM image of nano-particles collected at the upper grounded electrode for T_{on} =4.0 s. The image shows that the shape of nano-particles is spherical. From the TEM observation, we obtained a histogram of nano-particle size, as shown in Fig. 6. Their size distribution is well expressed by a Gaussian one having a mean size of 52 nm and a size dispersion of 10 nm. The mean size agrees fairly well with the size of nano-particles just before arriving the grounded electrode, measured by the LLS method. The small size dispersion suggests that spatial variation of their size is small.

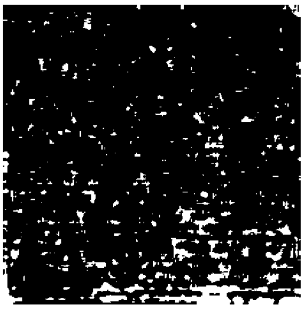

Fig. 5. TEM image of nano-particles.

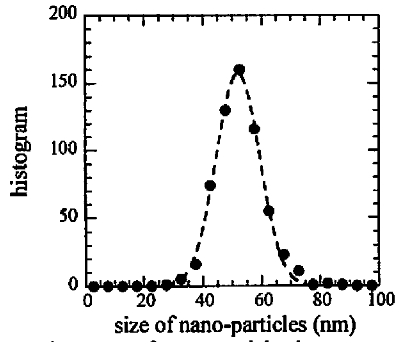

Fig. 6. Histogram of nano-particle size.

After turning off unmodulated discharges, nano-particles move away from their generation region towards the upper grounded electrode. Figure 7 shows trajectories of a position of the highest LLS intensity after turning off an unmodulated discharge. In the z-direction nano-particles move at a velocity of 6-9 cm/s for t =4-4.2 s and eventually they reach the upper grounded electrode at around t =4.2 s, while in the r-direction, they begin to move at a velocity of 8 cm/s at t =4.0s, then they slow down for t >4.1 s and stop near r =30 mm at t =4.6 s. After discharging off, motion of nano-particles is determined by the balance between thermophoretic force and gas viscous force [8]. Their velocity v_d is given by

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

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. To evaluate thermophoretic force exerted on nano-particles, we have measured spatial profiles of gas temperature using thermo labels and from the profiles we have deduced its gradient as shown in Fig. 8. The thermal gradient in the z-direction is 25 K/cm, while that in the r-direction is about 8 K/cm. Using the thermal gradient in the z-direction, v_d is evaluated to be 7 cm/s, which agrees well with the experimental value of 6-9 cm/s. Therefore, thermophoretic force mainly drives nano-particles towards the grounded electrodes after turning off discharges as shown in Fig. 4(a).

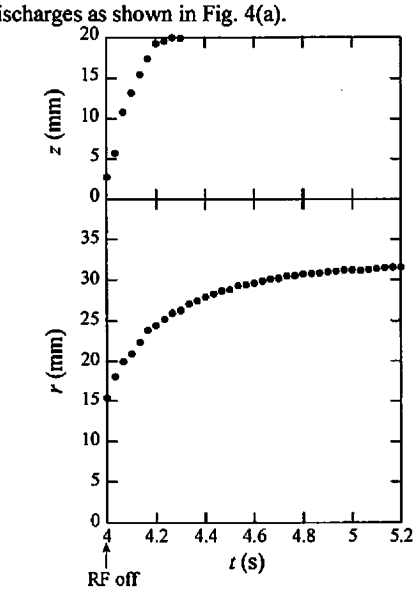

Fig. 7. Trajectories of a position of highest LLS intensity after turning off unmodulated discharge.

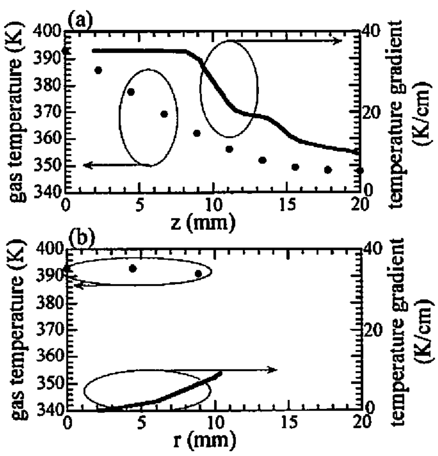

Fig. 8. Spatial profiles of gas temperature and its gradient in z-direction (a) and r-direction (b).

During the modulation period shown in Fig. 4(b), nano-particles are transported rapidly from their generation region towards the upper grounded electrode. Figure 9 shows classification of their transport region as parameters of T_{on} and Δt. The region for which the modulation has little effects on their transport is shown as A. The rapid transport for which a velocity is more than 60 cm/s is realized in the region C. The region B indicates the intermediate transport behavior region between A and C. The rapid transport is realized for Δt longer than a threshold Δt value and V_{AM} larger than a threshold V_{AM} value. Large nano-particles (long T_{on}) need long Δt to drive rapidly them towards the upper grounded electrode, probably due to their large inertia. Thus, two key parameters of the rapid transport are the discharge voltage and the period of the modulation.

Figure 10 shows spatial profiles of optical emission intensity and time averaged electrical potentials before and during modulation [9, 10]. At the beginning of the modulation, the width of the optical sheath near the powered electrode increases from 3.0 mm to 3.5 mm, within tens μs. Because of their large inertia, just after the modulation nano-particles charged negatively tend to remain in the sheath, and electrostatic force drives them towards the upper grounded electrode. Further study is needed to clarify the transport mechanism in detail.

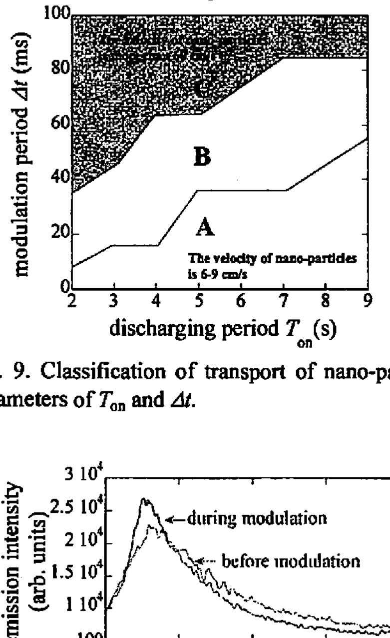

Fig. 9. Classification of transport of nano-particles as parameters of T_{on} and Δt.

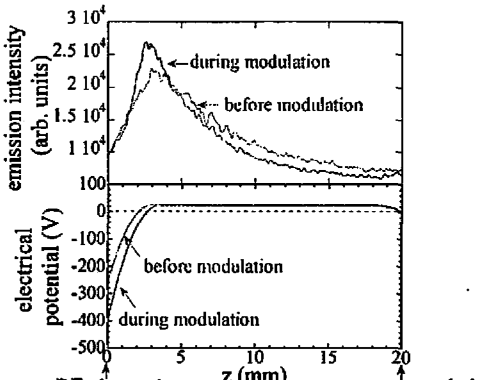

Fig. 10. Spatial profiles of optical emission intensity (a) and time averaged electrical potentials before and during modulation (b).

4. CONCLUSIONS

Transport of nano-particles in pulsed RF discharges has been observed using 2DLLS method. By using the modulation, nano-particles can be transported rapidly, at a velocity more than 60 cm/s, from their generation region towards the upper grounded electrode during the modulation period. Two key parameters of the rapid transport are the discharge voltage and the period of the modulation. The rapid transport is realized for Δt longer than a threshold Δt value and V_{AM} larger than a threshold V_{AM} value. The threshold Δt value increases with T_{on}, that is the size of nano-particles, probably due to their inertia.

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