Size determination of nanoparticles in low-pressure plasma with laser-induced incandescence technique

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We derive analytic formulas describing the temporal behavior of the laser-induced incandescence (LII) signal in both case of the heat transfer governed by radiation and collision. Using these formulas, we can describe the temporal behavior of the LII signal and determine the dimension of nanosize particles in low-pressure plasma. Simple calibration procedure is introduced for quantitative measurement of the particle size with the LII technique. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1599965]

Measurement of nanoparticle size is very important for process control in fabrication of microelectronic circuit devices and manufacturing various nanosize materials. In previous studies, there were several approaches to determining particle size based on laser diagnostics. Nowadays, the laser induced incandescence (LII) method is one of the most prevailing technique for particle size measurement in flames, which detects blackbody radiation from heated particles.[1,2] The LII signal has been analyzed with the time gate ratio method,[3] pyrometric determination of particle temperature after the laser heating based on the ratio of LII signals at two wavelengths,[4] and fitting the evolution of the full decay curve to LII model.[5]

Because of different environmental conditions related to the low-pressure processing plasmas, it is not appropriate that the theory of the LII technique for soot particle measurement in the flames is directly applied for measuring particle size in the plasmas. Since the dominant cooling process of the laser-heated particle in the low-pressure plasma is different to that in the combustion processes, the theoretical model of the LII signal from the heat balance equation results in different form involving thermal properties and temperature of the particle.

An attempt to determine the size of particles in the low-pressure plasmas was previously made with full-numerical approach solving the same governing equations of heat balance of the laser-heated particle.[6] It requires many unknown parameters to be used for fitting the overall LII decay signal to a theoretical model. However, most of the various material properties of the particles generated in the low-pressure plasma are unknown, and the heated particle temperature cannot be easily measured. The inappropriately measured or estimated particle temperature produces a critical error in particle size determined with the LII technique.

Therefore, for practical use of the LII technique in the low-pressure plasma, we need to develop a proper and easy model. In this letter, we derive simple formulas from the heat balance equations of the laser-heated particle, which describe the temporal behavior of the LII signal of particles in low-pressure plasmas. Fitting the decay curve of the LII signals to the formulas, we determine the dimension of nanosize particles in the low-pressure plasmas.

The general theory of the laser-induced incandescence technique is well described by Melton.[2]

$$\frac{dT}{dt}=\frac{qA_{\mathrm{abs}}}{c_s}-\frac{3h_c(T-T_0)}{\rho_s c_s a}-\frac{3N_v\Delta H_v}{\rho_s c_s a N_{Av}}-\frac{3\sigma_{\mathrm{sb}}(T^4-T_0^4)}{\rho_s c_s a}, \tag{1}$$

where q is the laser fluence, a is the particle radius, T_0 is the initial particle temperature, ρ_s is the particle density, c_s is the specific heat, σ_{sb} is the Stefan–Boltzmann coefficient, h_c is the convection coefficient, and A_{abs} $(=\{3K_{\mathrm{abs}}\}/\{4\rho_s a\}$, where K_{abs} is the absorption efficiency) is the mass specific absorption cross section. In Eq. (1), each term is the absorbed laser energy, the rate of heat transfer from dust particle to bulk plasma, the evaporation on the particle surface, and the rate of energy loss by Blackbody radiation, respectively.

Since the wavelength dependent emissivity $\epsilon(\lambda)$ equals the absorption efficiency $K_{\mathrm{abs}}(\lambda)$, the intensity of the emission spectrum from dust particles is given by[6]

$$I(\lambda)=\epsilon(\lambda)P(\lambda)=K_{\mathrm{abs}}(\lambda)P(\lambda), \tag{2}$$

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where $P(\lambda)$ is Planck function given as

$$P(\lambda)=\frac{2\pi c^2 h}{\lambda^5}\left[\exp\left(\frac{hc}{\lambda kT}\right)-1\right]^{-1}. \tag{3}$$

Here, h, k, and c denote Planck's constant, Boltzmann's constant, and the speed of light, respectively. If the size of the particles is assumed to be monodispersed, the time-dependent signal is integrated value via the finite Blackbody spectrum range ($\lambda_1 \leqslant \lambda \leqslant \lambda_2$) such as

$$S(t)=\int_{\lambda_1}^{\lambda_2}\left\{\frac{8\pi c^2 h\rho_s a A_{\mathrm{abs}}}{3\lambda^5}\left[\exp\left(\frac{hc}{\lambda kT(t)}\right)-1\right]^{-1}\right\}d\lambda, \tag{4}$$

and it can be expressed in logarithmic and time-derivative as following:

$$\frac{d}{dt}[\ln S(t)]=\frac{d}{dt}\left(\ln\int_{\lambda_1}^{\lambda_2}\left\{\frac{8\pi c^2 h\rho_s a A_{\mathrm{abs}}}{3\lambda^5}\times\left[\exp\left(\frac{hc}{\lambda kT(t)}\right)-1\right]^{-1}\right\}d\lambda\right). \tag{5}$$

Here, we introduce an approximation in the special range of $|\lambda_1-\lambda_2|\ll 1$:

$$\frac{1}{e^x-1}\approx\frac{C_2}{x^{C_1}} \quad \text{where,} \quad x\equiv\frac{hc}{\lambda kT}. \tag{6}$$

Here, C_1 and C_2 are constants, and Eq. (5) can be reduced as

$$\frac{d}{dt}[\ln S(t)]\approx\frac{C_1}{T(t)}\frac{dT(t)}{dt}. \tag{7}$$

This result is expressed in the function of the LII signal and particle temperature, and can be generalized for the determination of laser heated particle size in flame and plasma.

At low pressure and low laser fluence, therefore, because there is no laser absorption and evaporation loss is negligible in decay regime, the energy balance equation reduced to following simple expression:

$$\frac{dT}{dt}=-\chi\alpha p[T(t)-T_0(t)]-\frac{3\sigma_{\mathrm{sb}}[T(t)^4-T_0(t)^4]}{\rho_s c_s a}, \tag{8}$$

with

$$\chi=\frac{\gamma+1}{\gamma-1}\frac{1}{16\sqrt{T_0}}\frac{\sqrt{8k}}{\pi m}, \tag{9}$$

where m is the mass of the neutral gas atom, and the ratio of specific heats (γ) is 5/3 for monatomic ideal gases. In Eq. (1), the heat transfer loss in low pressure is introduced as $\chi\alpha p(T-T_0)$ according to the Knudsen theory.[6–8] Here p is neutral gas pressure and α is accomodation coefficient ($0<\alpha<1$).

In low-pressure plasma, the heat transfer of particles by collision is much smaller than that by radiation. Therefore, from Eq. (7) the time derivative of a integrated LII signal's logarithm is driven as

$$\frac{d}{dt}[\ln S(t)]=-\frac{3C_1\sigma_{\mathrm{sb}}[T(t)^4-T_0(t)^4]}{\rho_s c_s a T(t)}\approx-\frac{CT(t)^3}{a}, \tag{10}$$

$$C\equiv\frac{3C_1\sigma_{\mathrm{sb}}}{\rho_s c_s}. \tag{11}$$

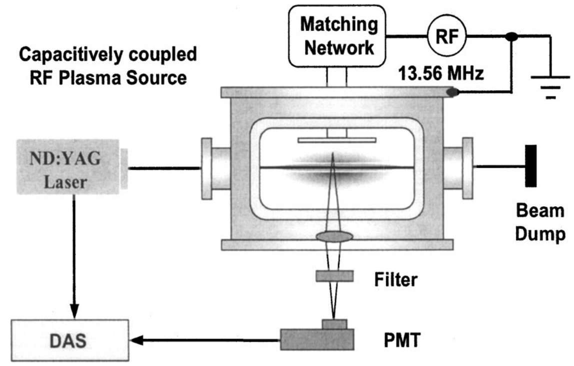

FIG. 1. Schematic diagram of experimental apparatus for nanosize particle detection with the LII technique. PMT—photomultiplier tube and DAQS—data acquisition system.

Here, we can successfully express the relation between particle size and LII signal at low pressure in the simple formula of Eq. (10). It is noticed that the slope is negatively proportional to the cube of particle temperature at a given particle size.

For the examination of the validity of Eq. (10) at the low pressure condition, the experiment was performed in 5% diluted $Ar-SiH_4$ plasma. A schematic diagram of experimental apparatus is shown in Fig. 1. Capacitively coupled plasma was generated with a 13.56 MHz rf source at the neutral gas pressure of 20 mTorr. The generated amorphous Si dust particles were irradiated by Nd:yttritium–aluminum–garnet (YAG) laser (Continuum PL9010) at 532 nm. The laser beam was collimated and beam diameter was 2 mm. The laser pulse width (full width at half maximum) was 8 ns and the repetition rate was 10 Hz.

The radiative heat transfer becomes relatively dominant process at low pressure. This fact results in the temperature dependency of the LII signal which is proportional to the cube of temperature evolution as shown in Eq. (10). In Fig. 2, it is found that the heat transfer by collision at low pressure is so small that the decay curve of temperature containing all terms duplicates that calculated without heat transfer by collision.

Figure 3 shows the logarithm of the measured LII signal at the laser fluence of 5.5 mJ. The signal was fitted to fourth-order polynomials of time with small residual. It was temporally differentiated and the result is shown in the same figure. The time-varying curve in Fig. 3 indicates that the slope of logarithm of the LII signal also decays in third-order polynomial temporally. Since particle size is not changed during the decay process and other parameters in Eq. (10) are constant, the measured slope is a function of the cube of the particle temperature.

In order to determine the particle size in low-pressure plasma with previous models,[3–6] we need to know the thermal properties of the particle material and the information of the temporal evolution of temperature of the particle. In practice, however, it is very difficult to properly estimate the thermal properties and the temperature evolution of the particle in low-pressure plasma. Equation (10) gives us a simple relationship among the particle size, the temperature evolution, and the thermal properties of material. First, since particle size is saturated after sufficient growth time, we measured the accurate size of the particles by taking scanning

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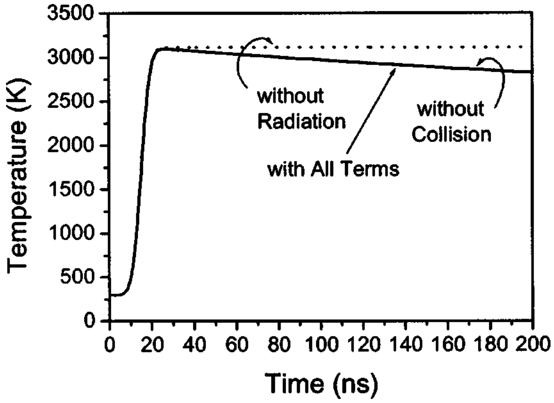

FIG. 2. Comparison of the relative contribution of heat transfer losses by collision and radiation in low-pressure plasma. The simulation was done with 0.3 mJ irradiation of 1064 nm Nd:YAG laser in 5% diluted $Ar-SiH_4$ plasma. The neutral gas pressure was 20 mTorr.

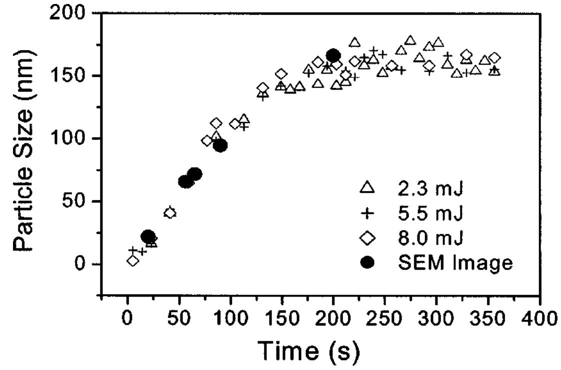

FIG. 4. Time evolution of dimension of the nanosize particle in the argon plasma detected with the LII technique. LII signals were recorded with the pulse laser energy of 2.3 mJ (△), 5.5 mJ (+), and 8.0 mJ (◇). The particle sizes determined with SEM images at corresponding evolution times are simultaneously plotted for comparison.

electron microscopy (SEM) images. By using the experimentally measured particle size, we determined the coefficient C in Eq. (10). Using Eq. (10) and a measured particle size, we fit a LII signal to the model to derive temperature evolution. After then, we put the obtained temperature evolution as a fixed parameter for the fitting to derive particle size. We continued the iteration with floating and fixing parameters of the particle size and the temperature evolution, alternatively. The iteration is readily converged in a few steps, giving unique solutions of the particle size and the temperature evolution. Second, we used this coefficient for fitting LII signals obtained in various experimental conditions and obtained the arbitrary particle size. It is noted that the distribution of the particle sizes determined by SEM was almost monodisperse.

Figure 4 depicts size of particle growing in 5% diluted $Ar-SiH_4$ plasma after the plasma is turned on. The LII signal was recorded with several laser pulse energy of 2.3 mJ (△), 5.5 mJ (+) and 8 mJ (◇). If we use higher laser pulse energy for the LII experiment, the temperature of the particle heated by the laser pulse become higher and we get a LII signal with different decay behavior. In the Fig. 4, we found the laser pulse energy does not affect much on the particle size measurement. In the experimental conditions shown in Fig. 4, the diameter change of the amorphous Si particles caused by the evaporation was roughly evaluated with full energy balance and mass conservation equations, and we found it is $<1\%$. We plot the particle size (●) determined

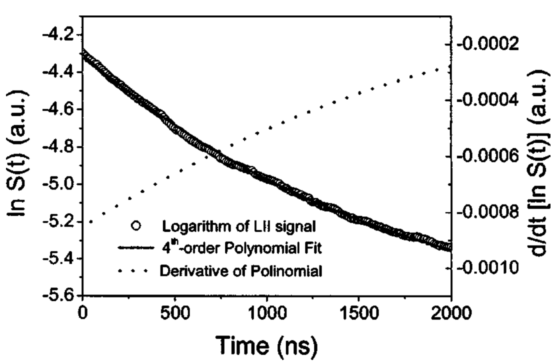

FIG. 3. The logarithmic expression of the measured LII decay signal (○) is fitted to fourth-order polynomial (solid line). The temporal derivative of the logarithm of the signal (dotted) was fitted to third-order polynomial. The energy of pulse laser used in the experiment was given by 5.5 mJ.

with SEM at several points in the same figure. For the calibration, we determined the coefficient C in Eq. (10) with the particle size in a SEM image taken at 200 s. It is found that all SEM data very well match to LII results. This means that the LII technique stably works with our analytical model. We estimated the overall uncertainty of the particle size determined in this work was less than 5%. We note that our model depend on neither the wavelength nor the energy of the excitation laser, but we need to choose the appropriate wavelength of the laser to meet the absorption of the particle material to get enough signal in the LII experiment. Since both the absorption and the emissivity of the nanosize particle depend on its size, the LII signal is strongly dependent on the size.

In conclusion, a method to determine the dimension of nanosize particle in low-pressure plasma with the LII technique is proposed and experimentally confirmed its validity. We extend the applicability of the LII technique to analyzing the size of nanoparticles that play one of main source of contamination in process plasmas. With aid of a simple analytical formula describing the relationship between size and temperature evolution of the particle, we obtain accurate information of the particle size by fitting the LII signal to the formula. It is found that the overall uncertainty in particle size measurement is less than 5%. It is remarkable that, without any material information of the particle, we can determine the dimension of nanosize particles generated in low-pressure plasma with the LII technique. It is well known that the distribution of the particle generated in many material processes and flames has often a log-normal functional form. We expect that our model can be extend to determine the size distribution of particles by integrating the LII signals emitted from particles of which size distribution has a functional form. Further, we expect that this technique can be applied to analyzing the nucleation process of nanosize particles in chemical vapor deposition for material synthesis.

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