Detection of dust particles in the plasma by laser-induced heating

W. W. Stoffels, E. Stoffels, G. M. W. Kroesen, and F. J. de Hoog
Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

(Received 4 October 1995; accepted 13 December 1995)

Heating of dust particles suspended in a low pressure discharge by means of a high power pulsed laser was analyzed. A detailed model of particle heating and thermal decomposition was developed and experimentally verified using 1 µm Teflon-like particles in a radio-frequency argon discharge. Laser-induced heating results in blackbody-like emission from the particles. This radiation can be easily recorded and a particle temperature of about 3500 K is determined by fitting the emission spectra. From the model it follows that the time resolved emission intensity gives valuable information about the particles: the time delay between the onset of the laser pulse and the blackbody-like emission corresponds to the heating time of the clusters and is dependent on their size. Moreover, the absolute emission intensity is proportional to the particle density. © 1996 American Vacuum Society.

I. INTRODUCTION

Particle formation in surface processing plasmas is now a widely recognized problem. As present research aims at full control of particle containing plasmas, one of the major experimental tasks is the determination of particle size and density. It is possible to determine the size of the particles by extracting and studying them outside the reactor, e.g., by scanning electron microscopy. However, in situ detection methods are more favorable as they allow one to study the particles in their natural environment and to exclude possible influences from outside the reactor. Absorption and scattering in the infrared region give information about size, density, and composition for relatively large clusters, but they are not sensitive enough to study particles smaller than 100 nm. The latter is, however, very essential from the point of view of understanding the growth kinetics of clusters in the discharge. Many previous studies were devoted to laser diagnostics of dust particles in plasmas. The commonly used method of laser light scattering is an experimentally easy technique. However, interpretation of the data in the Mie regime ($2\pi r/\lambda \approx 1$), with $r$ the particle radius and $\lambda$ the laser wavelength) is tedious and requires knowledge (or assumptions) of the refractive index of the material. For particles much smaller than the wavelength of the scattered light (i.e., in the Rayleigh scattering regime) the efficiency of scattering decreases drastically as the intensity is proportional to the sixth power of the radius ($I \approx r^6/\lambda^4$). Therefore other kinds of laser interaction with the particles can possibly provide a more sensitive detection technique.

Previously we studied laser-induced heating of the dust particles and proposed it as a new particle detection method. A pulsed high power laser is used to heat the particles and the subsequent bright white light emission is monitored by means of time resolved optical emission spectroscopy. The emission is a broad band continuum, which can be approximated very well by a blackbody spectrum at a temperature of about 3500 K. The wavelength integrated emission intensity is much stronger than the laser scattering signal. The ratio of blackbody to scattering intensity increases with decreasing particle size. There are some more advantages of detecting broad band emission, stray light, which disturbs scattering experiments, can here be easily eliminated. Moreover, the uniform angular distribution of the radiation is more convenient for detection.

In this article we present a detailed model, describing the observed phenomena during laser heating. Very good agreement is obtained between the theory developed and experimental data obtained in a rf argon plasma with a small CCl2F2 admixture, at a working pressure of 200 mTorr. The dust particles, formed in this discharge, were studied by means of in situ infrared absorption spectroscopy and ex situ scanning electron microscopy. The grains are relatively large (~1 µm) spheres, consisting mainly of a Teflon-like polymer (CF2). In the numerical analysis of the particle heating event we will substitute the well known physical properties of Teflon and argon.

The processes that occur during particle heating are discussed below. Further, a description of the experimental setup for laser heating is given. Finally, a comparison of the theory with the measurements is presented. It will be shown that the model developed accurately describes the observed phenomena.

II. THEORY

A. Energy balance of a heated particle

The temperature of particles in a plasma can be above ambient plasma temperature (~350 K), as its surface is heated by associating radicals and by ions, which recombine on the surface after being accelerated in the sheath surrounding the particle. We can assume that these processes are not important during laser–particle interaction as the energy flux provided by the plasma species is much lower than the laser fluence. For the sake of convenience we assume the steady state (initial) surface temperature of a particle to be 350 K. However, a slightly higher or lower initial temperature will not influence the conclusions.

When a laser beam strikes the cluster surface, energy is
absorbed, causing the particle to be heated. The absorbed laser energy is quasi-instantaneously converted into heat; the time of this local thermal relaxation is in the order of $10^{-12}$ s. In case of inhomogeneous absorption, thermal diffusion tends to establish a uniform temperature profile. Approximating the gradient length for thermal diffusion by the particle radius, the time constant for heat conduction within the particle can be expressed by $\tau = r^2/\chi$, where $\chi$ is the thermal diffusivity. For Teflon $\chi_{\text{F}} = 1.4 \times 10^{-7}$ m$^2$s$^{-1}$, which yields a time constant of 7 $\mu$s for a 1 $\mu$m Teflon particle. As the experiments are performed in the long pulse mode of a Nd:YAG laser, with a laser pulse length of 150 $\mu$s, it can be assumed that the temperature profile within a particle is uniform.

The absorbed laser energy is lost at the particle surface by radiation, heat conduction, and evaporation or thermal decomposition. The energy balance of a single cluster can be written as

$$\frac{1}{2} \pi r^3 \rho C \frac{dT}{dt} = \pi r^2 I_{\text{abs}} - 4 \pi r^2 (\Phi_{\text{con}} + \Phi_{\text{rad}} + \Phi_{\text{vap}}),$$

where $\rho$ and $C$ are the solid state mass density (kg m$^{-3}$) and heat capacity (J kg$^{-1}$ K$^{-1}$). The first term on the right-hand side describes the laser heating, where $I_{\text{abs}}$ is the absorbed laser fluence (W m$^{-2}$). The last three terms refer to energy losses: $\Phi_{\text{con}}$—conduction losses to the ambient gas, $\Phi_{\text{rad}}$—radiation losses, and $\Phi_{\text{vap}}$—losses due to evaporation or chemical decomposition of the particle material (all in W m$^{-2}$). In the following sections we shall estimate the time constants for these processes and compare their role in the heating event.

### B. Conductive losses

The first loss term ($\Phi_{\text{con}}$) in Eq. (1) refers to the thermal conduction losses. At low pressures, when the mean free path of neutrals in the plasma is much larger than the particle radius, the heat transport from the particle is described by the Knudsen theory:10,12

$$\Phi_{\text{con}} = \frac{c_p}{16(c_p/c_v - 1)} \frac{\rho}{T_g} \sqrt{\frac{8k_b}{\pi m_g}} \alpha \Delta T.$$  

(2)

Here $\rho$ is the gas pressure, $c_p/c_v$ its heat capacity ratio (5/3 for argon), $T_g$ and $m_g$ the temperature and mass of the gas atom/molecule, $\Delta T$ the temperature difference between the gas and the dust particle, and $\alpha$ is the accommodation coefficient (0 $<$ $\alpha$ $<$ 1).

A conduction loss time $\tau_{\text{con}}$ is given by

$$\tau_{\text{con}} = \frac{\rho C r^2}{3 \Phi_{\text{con}}}.$$  

(3)

Typical values for Teflon are $\rho = 2.2 \times 10^3$ kg m$^{-3}$ and $C = 10^3$ J kg$^{-1}$ K$^{-1}$. At 200 mTorr with the accommodation coefficient $\alpha$ equal to 1, the corresponding time constant for a 1 $\mu$m particle $\tau_{\text{con}}$ is 0.1 s. Since $\tau_{\text{con}}$ is much longer than the laser pulse (150 $\mu$s), conduction losses to the ambient gas during the particle heating can be neglected in low pressure plasmas.

### C. Light absorption and emission by particles

Several regimes in the light scattering, absorption, and emission of particles can be distinguished, dependent on the Mie parameter $x = 2 \pi r/\lambda$. For particles that are large with respect to the wavelength ($x \gg 1$), linear optics and bulk physics can be used, e.g., for absorbing clusters an estimate of size and/or density based on a simple extinction measurement. For intermediate sizes ($x$ in the order of 1) the more complicated Mie theory describes particle–light interactions.13 For particles much smaller than the wavelength the Rayleigh theory applies. The scattered and absorbed intensities ($I_\text{sca/abs}$) are described by scattering and absorption efficiencies ($Q_\text{sca/abs}$):

$$I_{\text{sca/abs}} = Q_{\text{sca/abs}} I_0,$$

where $I_0$ is the incident laser fluence (W m$^{-2}$). For 1 $\mu$m particles, studied in this work, $Q_{\text{abs}} \approx 1/2$ has been taken.13 For small particles ($x \ll 1$):

$$Q_{\text{sca}} = \frac{8}{\pi} \frac{x^4}{n^2 + 2} \quad \text{and} \quad Q_{\text{abs}} = -4 \pi x \text{Im} \left( \frac{n^2 - 1}{n^2 + 2} \right),$$

where $n$ is the complex refractive index of the particle material. Thus the scattered intensity decreases as $r^6$. On the other hand, the absorbed intensity depends on $r^3$. In terms of macroscopic properties this implies that for small particles homogeneous volume heating occurs, while for larger particles only the surface is heated and consequently the absorbed intensity depends on $r^2$. The large difference in the size dependence between scattering and absorption makes all methods based on laser absorption interesting for the detection of small opaque clusters.

The emission spectrum of small clusters is not a black-body, but it is related to a blackbody through the wavelength dependent emissivity $[\epsilon(\lambda)]$. This is defined as the ratio of the actual intensity emitted by the particle [$I(\lambda)$] and the blackbody intensity, given by the Planck function [$P(\lambda)$]:

$$P(\lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_b T}\right) - 1}.$$  

(6)

Here $h$, $c$, and $k_b$ denote Planck’s constant, the velocity of light, and Boltzmann’s constant, respectively. Of course $\epsilon(\lambda)$ is smaller than 1. Using the principle of microscopic reversibility, it can be shown that for small particles the emissivity $\epsilon(\lambda)$ equals the absorption efficiency $Q_{\text{abs}}$ given by Eq. (5).14 The emission intensity of a small particle can therefore be approximated by

$$I(\lambda) = \epsilon(\lambda) P(\lambda) = Q_{\text{abs}}(\lambda) P(\lambda).$$  

(7)

As $Q_{\text{abs}} \sim \lambda^{-1}$, the wavelength dependence of the continuous emission of small particles, like nanoscale silicon clusters formed in a SiH$_4$ plasma, is given by $P(\lambda)/\lambda$, a “Planck continuum” shifted to the blue.
D. Heating and evaporation model

A simple kinetic equation for the particle temperature, containing only the laser heating and radiative losses, reads

\[
\frac{1}{2} r \rho C \frac{dT}{dt} = Q_{\text{abs}} I_0 - 4 \epsilon \sigma_s T^4.
\]

This equation can be solved numerically after introducing the experimentally determined time behavior of the laser fluence. The time behavior of the particle temperature during the laser pulse, calculated using Eq. (9), for an average laser fluence of \(I_0 = 8 \times 10^8 \text{ W m}^{-2}\) and \(r = 1 \mu\text{m}\) is shown in Fig. 1. It can be seen that the temperatures, reached at this laser energy, are unrealistically high. As no solid material can withstand these temperatures the clusters will start to evaporate or decompose at a much lower temperature. This decomposition will introduce an additional loss term in the energy balance and prevent such overheating.

The energy losses due to particle evaporation or thermal decomposition can be related to the decrease rate of the particle radius: \(\Phi_{\text{vap}} = H/V_m (dr/dt)\), where \(H\) is the energy of the decomposition process (\(1/\text{released molecule}\)) and \(V_m\) (\(\text{m}^3/\text{molecule}\)) the molecular volume in the solid state \((V_m = M/\rho\), where \(M\) is the molecular mass of the released fragment). The final energy balance for a particle can be now written as

\[
\frac{1}{2} r \rho C \frac{dT}{dt} = Q_{\text{abs}} I_0 - 4 \epsilon \sigma_s T^4 - \frac{H}{V_m \frac{dr}{dt}}.
\]

In the initial phase of particle heating the loss terms can be neglected. From the above an estimate for the heating time \(\tau_{\text{heat}}\) can be obtained:

\[
\tau_{\text{heat}} = \frac{4 \rho C \Delta T}{3 Q_{\text{abs}} I_0}.
\]

When a particle is heated up to a sufficiently high temperature, evaporation or decomposition becomes important. The flux of evaporated material from the particle surface is given by \(n_c c/4\) where \(c = (8 k_B T / \pi M)^{1/2}\) and \(n_c\) is the density of the evaporated material at the cluster surface. The surface density \(n_c\) can be related to the surface temperature by the equilibrium Clausius–Clapeyron relation:

\[
n_c k_b T = B \exp(-\theta/k_b T).
\]

Here \(\theta\) and \(B\) are material dependent integration constants, \(\theta\) reflects the energy needed to release a molecule from the surface, and \(B\) the saturated vapor pressure. In our case there is no equilibrium between evaporation and vapor condensation, but it is still plausible to assume an analogous expression for the vapor pressure; only the constant \(B\) will be different from the “saturated vapor pressure.”

Using Eq. (12) and replacing \(\theta\) by the decomposition energy \(H\), the final kinetic equation for the particle radius can be derived:

\[
\frac{dr}{dt} = V_m c \frac{c}{4} n_c = V_m \frac{c}{4} k_b T \exp(-H/k_b T).
\]

In order to simulate the evaporation/decomposition process, Eqs. (10) and (13) will be integrated numerically. From the obtained temperature and radius the time dependent blackbody emission intensity will be calculated and compared to the measured intensity. The constants \(H\) and \(B\) have to be determined by fitting the experimental data. We note, however, that the Teflon-like particles most likely decompose into \(\text{CF}_2\) fragments as the energy needed to break a \(\text{C}–\text{C}\) bond is only about 3.5 eV, while the energy of the other bonds is higher (e.g., \(\text{C}–\text{F}\) with 4.8 eV). Therefore we expect that the decomposition energy \(H\) is close to 3.5 eV.

III. EXPERIMENTAL CONDITIONS

The measurements on particle heating described in Sec. IV were performed using a Quanta Ray DCR-11 Nd:YAG laser. The laser was operated mainly in the long pulse mode at 1064 nm. In this mode the laser pulse consists of a train of short (~1 \(\mu\)s) pulses, spread over about 150 \(\mu\)s. Occasionally, the laser has also been operated in a \(Q\)-switched mode, which results in a single 8 ns pulse. The maximum available pulse energy in both cases is about 0.5 J. The “donut” shaped laser beam is collimated into a pencil-like beam of 2 mm in diameter by means of two lenses and fired through the plasma at a variable distance from the electrodes. For the long pulse mode this results in a maximum laser intensity \(I_0 = 1.1 \times 10^9 \text{ W m}^{-2}\), averaged over the pulse duration.
Typically, the experimental data were obtained by averaging the emission over 25 laser shots. In order to avoid signal attenuation due to particle destruction in the laser beam, the laser repetition frequency has been kept below 1 Hz. This is sufficiently low for a complete particle redistribution and the removal of the evaporated material to the pumps. The time resolved emission spectra of the particles are recorded using an EG&G OMA III system. The time resolved visible emission intensity is recorded using a photodiode and a digital oscilloscope.

The particles are formed in a plasma, containing 5% CCl₂F₂ in argon, at a total pressure of 200 mTorr, rf input power of 100 W, and total flow rate of 30 sccm. A 10 cm silicon wafer is placed on the lower, water cooled rf electrode. A detailed description of particle formation and its properties under these conditions is given elsewhere. The measurements were performed after 30–60 min of plasma operation. On this time scale only long term fluctuations in particle size and density occur. The average particle radius is about 1 μm. Some experiments were performed in a “dusty” argon plasma (i.e., a pure argon plasma obtained by closing the CCl₂F₂ flow in an Ar/CCl₂F₂ plasma). In this case particles of various sizes are present in the plasma. Close to the powered electrode relatively large particles are accumulated (r > 1 μm), these have been detected by He–Ne scattering and infrared spectroscopy. However, laser-induced heating also allows one to detect smaller particles that are spread over the whole dusty argon plasma and cannot be seen by He–Ne scattering.

IV. RESULTS AND DISCUSSION

The wavelength integrated emission intensity as a function of time is shown in Fig. 3. Laser stray light, displaying the actual laser pulse shape, is collected on the window and given for comparison. A delay between the start of the laser pulse and the continuum emission is evident. This is consistent with the above described heating theory. Equation (11) predicts a heating time of about 25 μs for a 1 μm cluster heated to 3600 K at a laser fluence of 8×10⁸ W m⁻². However a more accurate value for the heating time can be obtained by fitting the whole emission curve with numerical solutions of Eqs. (10) and (13). For this purpose the measured time dependence of the laser fluence is used (Fig. 3). The calculations are performed for r = 1 μm, corresponding to the scanning electron microscopy data. The fit parameters are H and B. The particulate radius determines the heating time: the time delay of the maximum laser-induced emission

![Fig. 2. A scheme of the optical emission setup used to study the laser–particle interactions. The collimated beam of a Nd:YAG laser is used to heat the particles. The time resolved spectra are collected using an EG&G OMA III system. The time resolved visible emission intensity is recorded using a photodiode and a digital oscilloscope.](image)

![Fig. 3. Wavelength integrated laser-induced emission (~300–1000 nm, with a KG 3 filter) from the particles under standard plasma conditions (solid curve) and normalized laser stray light (dashed curve), measured using the fast diode (averaged over 25 laser shots). The time averaged laser fluence is 8×10⁸ W m⁻².](image)

![Fig. 4. Wavelength integrated (~300–1000 nm) laser induced emission (dots), measured with the fast diode in combination with a KG 3 filter and the numerical fit (solid curve), obtained using Eqs. (10) and (13). The average laser fluence is 8×10⁸ W m⁻². The calculations are performed for a 1 μm particle. The onset of the laser pulse is at t = 0 s.](image)
signal with respect to the onset of the laser pulse. The decomposition energy $H$ is chosen so as to accommodate the experimentally determined particle temperature ($\sim 3600$ K). Finally, $r$ and $B$ determine the decay of the emission due to the decrease of the particle radius in time. In Fig. 4 the experimental and theoretical emission curves as a function of time are plotted. It can be seen that an excellent fit is obtained for $B=4.2 \times 10^8$ Pa and $H=3$ eV. The time dependence of the particle radius and temperature are shown in Fig. 5. It can also be seen that the measured time behavior of the temperature is reproduced well by the model. The temperature does not significantly change in time as long as decomposition takes place. The energy losses due to decomposition are so high that they balance the absorbed laser energy. As a result, $dT/dt=0$ in Eq. (10). The radiation losses during the entire event are negligible.

The validity of the proposed model was checked by recording the emission curves for several laser fluences. In Fig. 6 the emission curve is shown for a lower laser fluence. In this case the heating time is significantly longer. Also, the decay time of the emission is longer because the particles evaporate slower, as can be seen in Fig. 7. Note that the scale for the particle radius in Fig. 7 is different from the one in Fig. 5. The rise time of the signal for several laser fluences, obtained by fitting the measured data with the numerical solutions, is shown in Fig. 8. For laser fluences below $10^8$ W m$^{-2}$ the heating time becomes longer than the laser pulse duration. The emission is then drastically reduced.

The total emission intensity was determined from the OMA spectra as a function of laser fluence for three different plasma conditions (see Fig. 9). The corresponding temperatures are shown in Fig. 10. The emission intensities vary over several orders of magnitude, depending on plasma conditions, but the temperatures are in all cases almost the same. This is an indication that the physical properties of particles do not depend on the dusty plasma conditions. The dashed curves in Figs. 9 and 10 are the dependences predicted by the model. Again, very good agreement with experimental data is obtained. The temperature increases strongly with laser fluence.
fluence until the temperature is reached, at which decomposition becomes important (about 3000 K at 10^8 W m^{-2}). For fluences higher than this threshold value only a weak temperature increase is found. The decomposition speed increases linearly with the laser power, which implies that at high fluences the particles are destroyed faster and consequently the duration of the entire event is shorter. Therefore it is not surprising that the time integrated emission at high fluences saturates and eventually decreases, as is shown in Fig. 9.

From this observation it follows that a laser with an extremely high power is not necessarily efficient in inducing an intense blackbody-like radiation from particles. This is in agreement with the experiments with a Q-switched laser (pulse duration ~ 8 ns). Typically we have observed a 100–1000 times lower emission at the same laser energy per pulse. In this case the surface heating and destruction are extremely fast, but the irradiated intensity is limited due to the fact that the destruction process occurs at an almost constant temperature. Small particles, which are heated homogeneously, are destroyed immediately, while for larger particles only the outer layer is heated by the laser, as internal thermal conduction is not fast enough to provide a homogeneous temperature profile within a particle. After the laser pulse the remaining particles will cool down by internal heat conduction within less than 1 μs. Therefore the upper limit for the duration of this event is about 1 μs. In comparison with the emission from a 150 μs long pulse, it is clear that the total emission is much lower. Thus in order to obtain the optimal detection limit for the technique described in this work the laser pulse should be as long as possible and the absorbed intensity should, after heating the particles, only balance the
radiative losses at a temperature just below 3500 K to prevent particle destruction. Note, however, that in this case the additional information, provided by the decomposition kinetics, would be lost.

It was already mentioned that for large particles, which are surface heated, the heating time is a function of the cluster radius. The radius of such particles can thus be easily determined from the measured emission curve. Needless to say, the emission intensity is proportional to the particle density, so this technique allows one to determine both size and density from a single measurement (provided absolute intensity measurements are performed and a necessary calibration is made to account for unknown material constants). This makes laser heating a very valuable diagnostic. In Fig. 11 the calculated emission curves (normalized to the particle surface, $r^2$) are shown. Both the rise time and the decay time of the laser-induced emission are size dependent. In Figs. 12 and 13 the corresponding temperatures and radii are plotted. It is clear that smaller particles are heated and decomposed faster. For very large particles ($r > 2 \mu m$) the heating time is so long that the decomposition temperature is not reached during the laser pulse. Therefore the emission intensity from these particles is relatively low (Fig. 11) and their radii stay constant in time (Fig. 13). Finally, it should be noted that, although for smaller particles, for which $Q_{abs} \sim r$ the heating time becomes size independent, the destruction kinetics and consequently the decay time of the laser-induced emission can provide information about the particle radius $r$. It was shown by Boufendi et al.\textsuperscript{15} that this method can be applied very well to nanoscale silicon particles. By fully evaporating the particles with a XeCl laser at $\lambda = 308$ nm an $r^3$ dependence of the time and wavelength integrated emission intensity on the particle size was found. This is more favorable than the $r^6$ dependence of the scattering intensity in the Rayleigh regime.

**V. CONCLUSIONS**

Interactions of a high power laser with dust particles, suspended in a low pressure radio-frequency plasma, were studied in detail. The particles are heated to their decomposition temperature, and time and wavelength resolved blackbody-like radiation from the heated clusters is detected. The time evolution of this laser-induced emission is delayed with respect to the onset of the laser pulse. This delay is due to heating of the clusters and it depends on laser fluence and particle size. It can be used to determine particle size, while the total emission intensity is proportional to the particle density. The time resolved spectra yield typical temperatures of 3500 K, independent of the plasma conditions. The temperature and the emission intensity saturate with the laser fluence due to thermal decomposition of the particles. A model for laser light absorption, heating, and decomposition of the clusters was developed. This model gives a very good description of the observed phenomena; the time dependent emission signal can be fully simulated. Moreover, the dependences of laser-induced emission intensity and particle temperature on laser fluence are predicted.

The laser-induced heating of particles forms a powerful \textit{in situ} detection method, allowing one to determine particle size and density from a single measurement. Moreover, it was shown to be more sensitive than laser light scattering, especially for clusters much smaller than the laser wavelength.

---


\textsuperscript{12}M. Knudsen, Ann. Phys. (Leipzig) 34, 593 (1911).


\textsuperscript{14}C.F. Bohren and D.R. Huffman, \textit{Absorption and Scattering of Light by Small Particles} (Wiley, New York, 1983).