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Laser-Particulate Interactions in a Dusty RF Plasma

E. Stoffels, W. W. Stoffels, D. Vender, G. M. W. Kroesen, and F. J. de Hoog

Abstract—The interaction of particulates formed in an argon RF discharge containing 1–5% CCIF2 admixture with a pulsed infrared laser (Nd:YAG, intensity \( \sim 10^5 \text{ W} \cdot \text{m}^{-2} \), pulse duration \( \sim 10^{-4} \text{ s} \)) has been studied in situ. The white light emitted during this process has been monitored as a function of time and wavelength using a fast photo diode and an optical multichannel analyser. The spectra have been fitted with blackbody curves with a standard deviation of 5%. A spectral temperature of about 3500 K has been obtained for various plasma conditions and attributed to the decomposition temperature of the particulate material. A model based on laser heating, internal heat conduction and chemical decomposition is compared with the experimental results. This model predicts the time constants for heating and decomposition of the particulates and explains the dependence of the measured emission intensity on the laser intensity.

I. INTRODUCTION

Small dust particulates have been observed in a wide variety of semiconductor processing plasmas [1]–[3]. These grains, ranging in size from several nanometers to millimeters cause severe damage to devices fabricated by plasma processing. As advanced semiconductor technology aims at fabricating very small structures, it is necessary to avoid formation of even the smallest grains in the reactor. On the other hand, abundant particulate formation in several discharges suggests a new application of these plasmas as particulate sources, delivering grains with a desired size and physical properties. In both cases an in situ measurement of the particulate size and density is required. Commonly applied light scattering is an experimentally easy technique, but its efficiency decreases drastically for particulates much smaller than the wavelength of the scattered light. In the Rayleigh scattering regime the intensity is proportional to the sixth power of the radius. However, other kinds of laser interaction with the particulates can possibly provide a more sensitive detection technique.

A high power infrared laser (Nd:YAG) has been used for the destruction of particulates in an argon/CCIF2 RF plasma [4]. The laser-particulate interaction is followed by bright, white light emission. A comparison with light scattering has revealed that this emission is at least 10 times more intense than scattering at 90° and the intensity ratio of these signals increases with decreasing particulate size. There are some more advantages of detecting the broad band emission. The stray light, which disturbs the scattering experiments can be easily eliminated here. Moreover, a uniform angular distribution of the radiation is experimentally more convenient for detection.

In this work we study the emission, following the laser destruction of particulates, by means of time resolved optical emission spectroscopy. Most physical properties of these particulates are unknown. However, considering the composition of the gas and the infrared absorption spectra we can assume, that they are teflon like polymers (CF2)x [5]. In the estimates made below the physical properties of teflon are taken and particulates are assumed to be spherical.

II. THEORY

The initial particulate temperature can be slightly above the ambient plasma temperature (\( \sim 300 \text{ K} \)) as its surface is heated by bombarding ions accelerated in the sheath surrounding the particulates. When a laser beam strikes the cluster surface, laser energy is absorbed, causing the particulate to be heated. Heat conduction within the particulate will homogenize the temperature distribution. Energy is lost at the surface by radiation, evaporation or thermal decomposition and conductive losses.

The place and time dependent energy balance within a particulate can be written as:

\[
\frac{\partial T}{\partial t} = \frac{\kappa}{\rho C} \Delta T + \nabla \cdot (K \nabla T) - \delta r - \Phi_{\text{rad}} - \Phi_{\text{con}} - \Phi_{\text{evap}}
\]

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, with \( \kappa \)-absorption coefficient in the solid state (m\(^{-1}\)), I-laser intensity (W-m\(^{-2}\)), \( 1 - R_0 \) the angle dependent fraction of the laser intensity penetrating the particulate and \( d \)—the optical path length of a laser photon at a given point within the particulate. The second term represents the heat conduction within the particulate (\( K \)—thermal conductivity). The last three terms refer to surface processes (denoted by the Dirac delta function) at \( r = a \), where \( a \) is the radius of a particulate: \( \Phi_{\text{rad}} \)-radiation losses, \( \Phi_{\text{con}} \)-conduction losses to ambient gas and \( \Phi_{\text{evap}} \)-losses due to evaporation or chemical decomposition (all in W-m\(^{-2}\)).

Based on this formula several estimations can be made. First we have to note that if we expect the particulates to emit blackbody like radiation, the optical depth for a single particulate (\( \kappa \cdot a \), must be at least 10. Together with a typical size of a particulate (0.1–1 \( \mu \)m), estimated from the ratio of forward and perpendicular He-Ne laser scattering, this gives us a lower limit for the absorption coefficient of \( 10^7–10^8 \text{ m}^{-1} \), which is a realistic value for opaque materials. Therefore the total power deposited in a particulate by the laser is simply...
\[ \pi a^2 \cdot (1 - R)I, \text{ where } RI \text{ denotes the total scattered intensity.} \]

Note that in case of such a high absorption by a single particulate the laser intensity would be seriously attenuated in the plasma even for very small \( R \). Since we observe an attenuation \((A)\) of about 1% over the whole plasma length \((L)\), this gives us an estimate of the particulate number density:

\[ N = \frac{A}{\pi a^2 \cdot L} \]  

Substituting \( L \approx 0.2 \) m it gives \( 10^{10} - 10^{12} \) m\(^{-3}\) for particulates between 0.1 and 1 \( \mu \)m.

Further we note that for absorbing particulates with \( \alpha \) in the order of the wavelength the reflection coefficient is about 1/2 [6]. For smaller particulates \((\alpha < \lambda)\) the scattered intensity \((R)\) decreases as \( \alpha^6 \). The absorbed intensity on the other hand depends on \( \alpha^2 \) when \( \alpha > \kappa^{-1} \) and on \( \alpha^3 \) when \( \alpha < \kappa^{-1} \) and homogenous volume heating occurs. This feature makes laser absorption interesting as a detection technique for small opaque clusters. Even though for smaller particulates the emission spectrum deviates strongly from blackbody, other radiative processes (fluorescence, photoluminescence) can be useful for cluster detection.

Some other simplifications of the energy balance (1) can be made by estimating typical time constants for thermal conduction losses. This can be done by introducing appropriate gradient lengths in a heat conduction equation. A time constant for heat conduction within the particulate can be expressed by:

\[ \tau_{in} = \frac{\rho C a^2}{3K}, \text{ where the gradient length is estimated by the particulate size } a. \]

The characteristic time of the energy loss by thermal conduction to the ambient gas \((\Phi_{e})\) is:

\[ \tau_{in} = \frac{\rho C a^2}{3K_{amb}}, \]

Here \( \Lambda \) is the gradient length, which we approximate by the mean free path for neutrals in the ambient gas and \( K_{amb} \) is the thermal conductivity of the gas. Substituting the typical values for teflon: \( \rho = 2.2 \cdot 10^3 \text{ m}^{-3} \), \( C = 10^3 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \), \( K = 0.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \), and \( \Lambda \approx 0.3 \text{ mm} \), we find \( \tau_{in} \approx 2 \cdot 10^{-9} \) s and \( \tau_{out} \approx 10 \) ms  for a 1 \( \mu \)m particulate. This implies that at the time scale of the laser pulse (100 \( \mu \)s), the internal heat conduction provides a uniform temperature profile within a particulate, while the heat losses to the ambient gas can be neglected.

The energy losses due to particulate evaporation or thermal decomposition can be related to the decrease rate of the particulate radius:\( \Phi_{e} = H/V_m \cdot (da/dt) \), where \( H \) is the energy of the decomposition process \((J \cdot \text{mol}^{-1})\) and \( V_m \) the molar volume \((m^3 \cdot \text{mol}^{-1})\). Using the above simplifications and substituting Wien’s displacement law for the radiative losses the energy balance (1) integrated over the particulate volume can be written as:

\[ 4/3\pi \rho C \frac{da}{dt} = (1 - R)I - 4 \sigma \varepsilon a^4 - 4 \frac{H}{V_m} \frac{da}{dt} \]

\[ (3) \]

where \( \sigma \varepsilon = 5.67 \cdot 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4} \) and \( \varepsilon \) is the integrated emissivity. In the initial phase of particulate heating the loss terms can be neglected. A simple expression for the heating time \((\tau_{\text{heat}})\) is therefore:

\[ \tau_{\text{heat}} = \frac{4 a \rho C \Delta T}{3(1 - R)I} \]  

\[ (4) \]

When a particulate is heated up to a sufficiently high temperature, evaporation or decomposition become important. Assuming a constant temperature during this process, the time dependent behavior of the particulate radius is:

\[ \frac{da}{dt} = \frac{V_m}{4H} ((1 - R)I - 4 \sigma \varepsilon a^4) \]

\[ (5) \]

The above formulas will be used to estimate the heating and destruction rates for our particulates.

### III. EXPERIMENTAL SETUP

The capacitive coupled discharge has been operated at 13.56 MHz by an ENI ACG-3 radio frequency generator with an ENI 5 matching network optimizing the power dissipation in the plasma. The maximum power input is 120 W. The plasma is sustained between two parallel aluminum plates (diameter—12 cm, separation—5 cm). A 10 cm Si wafer is placed on the lower RF electrode. The argon/CCl\(_2\)F\(_2\) mixture is introduced homogeneously through a slit around the RF electrode (see Fig. 1). Typical dusty plasma conditions are: 1.5 sccm (about 5%) CCl\(_2\)F\(_2\) and 28.5 sccm Ar flow at a total pressure of 27 Pa and power input of 100 W. The measurements have been performed after 30 to 60 min of plasma operation, when only long term fluctuations in particulate density occur.

The particulate destruction has been performed using a Quanta Ray DCR-11 Nd:YAG laser. The laser has been operated mainly in the long pulse mode at 1064 nm. In this mode the laser pulse consists of a train of short (ca. 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 20 ns pulse. The maximum available pulse energy in both cases is about 0.4 J. The donut shaped laser beam is collimated into a pencil-like beam of 2 mm 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 \( I = 8.5 \cdot 10^8 \) W \cdot m\(^{-2}\).
laser pulse, focused by two lenses in a parallel beam, heats the particulates $pc$, Fig. 2. A scheme of the optical emission setup. After a lens-fiber system. The wavelength selected light is detected by the gated diode array of the OMA, resulting in a time and wavelength resolved signal.

The time resolved wavelength integrated emission intensity has been measured using a fast photo diode in combination with a high pass filter (KG 3) has been used to discard scattering and stray light at 1064 nm. In order to collect time resolved spectra the emission has been imaged using a quartz lens on a quartz fiber guiding it to a 25 cm grating. Finally the light signal has been detected by a gated intensified diode array which is part of an optical multichannel analyzer (OMA, EG&G model 1461). The transmission of the optical system and the sensitivity of the diode array have been determined using a tungsten ribbon lamp. This correction has been incorporated in all data. Since the gain of the diode array decreases rapidly in the near infrared region, only visible emission (up to 800 nm) could be collected. The background plasma radiation has been subtracted from the measured spectra.

IV. RESULTS AND DISCUSSION

The radiation caused by the particulate interaction with a strong infrared laser beam consists practically only of continuum. No atomic or molecular line (band) emission has been found, even in the extinction phase. The shape of this continuum is best approximated by a Planck blackbody curve with a temperature around 3000 K. A typical spectrum and its fit are shown in Fig. 3. The standard deviation of the Planck curve fit for the majority of spectra does not exceed 5%. Only for weak signals in the late extinction phase the standard deviation increases up to 10%. Similar blackbody like spectra have been found by Geogehan for particulates produced by laser ablation of a solid [7].

The wavelength integrated emission intensity as a function of time is shown in Fig. 4. Laser stray light collected on the window, displaying the actual laser pulse shape is given for comparison. Fig. 5 shows the detailed time resolved structure of these two signals. It can be seen that though the laser-induced visible emission roughly follows the infrared laser signal, it does not display the short pulse time structure of the stray light (Fig. 5). This is in agreement with the blackbody character of the emission and it is essentially different from the light normally observed from a laser-induced plasma above a solid surface. In the latter case the emission, containing line (band) radiation as well as free-free continuum (Bremstrahlung), decays rapidly within the first microsecond after the laser pulse [8], [9]. In our pressure range the plasma itself can by no means emit blackbody like radiation. The vapor cloud, generated by the laser destruction of the particulates is also unlikely to do so, as it quickly becomes optically thin while expanding. The absorption coefficient of an expanding cloud decreases with increasing cloud volume ($\kappa \sim \rho^{-2}$), which implies that the optical depth decreases as $\rho^{-2}$ with the cloud radius. Since the expansion speed, corresponding to the surface temperature of the particulate is approximately 1000 m/s in our conditions, the optical depth of a cloud is 100 times lower than this of a solid ($\rho \sim 1 \mu m$) after only 10 ns. From this cloud free free, free bound or bound bound emission can be expected but not a blackbody like continuum. Therefore we can state that the observed blackbody emission originates from the surface of the heated particulates and consequently it delivers information about their heating and destruction kinetics.

An interesting aspect of the time dependent behavior of the continuum radiation (Fig. 4) is a 30 $\mu$s delay between the fast
rising laser pulse and the maximum visible emission. A first guess is that it is caused by a slow laser heating. Indeed, (4) predicts a heating time of about 40 µs for a 1 µm cluster heated up to 3000 K at the laser energy of 0.2 J (4 · 10^8 W·m⁻²). However, the temperature, obtained by fitting the time resolved spectra (Fig. 6), is high already at the onset of the laser pulse. This effect can be attributed to a broad particle size distribution. From (4) follows that small particulates are heated faster and as the emission intensity of a blackbody is inversely proportional to \( \exp(h\nu/kT) - 1 \) only the hottest particulates have a significant contribution to the observed spectrum, even if their emitting surface is small. Therefore the emission just at the onset of the laser pulse originates from small particulates, which are heated very fast to the decomposition temperature. The maximum emission intensity corresponds to particulates with a larger emitting surface and it is reached after the larger clusters have been heated.

If we assume the integrated emissivity (\( \epsilon \)) to be 1 (perfect blackbody), the radiative losses (\( 4\pi a^2\sigma T^4 \)) at the highest measured temperature of 3700 K are \( 10^{-4} \) W, which is a small fraction of the laser power absorbed by the 1 µm particulate (\( \pi a^2 \cdot (1 - R)I \sim 10^{-3} \) W for 0.3 J/pulse). Thus after the particulates are heated the major part of the laser energy is consumed in the decomposition process. If we use a teflon-like structure this process is thermal decomposition (presumably into CF₂ fragments) rather than evaporation. We estimate the decomposition energy by the energy needed to break a C-C bond (about 3.5 eV). Substituting this into (5) we obtain a decomposition rate of \( da/dt \sim 10^{-2} \) m/s at 10⁹ W·m⁻². This implies that a 1 µm particulate of 100 µs is decomposed within about 100 µs. Consequently, most particulates within the laser volume are destroyed during the laser pulse, especially at higher laser energies.

The total emission intensity has been determined as a function of the laser energy for three different plasma conditions (see Fig. 7). A threshold energy of about 0.03 J/pulse (6·10⁷ W·m⁻²) is needed for the initiation of this laser-induced process. This energy corresponds with heating a 1 µm particulate to about 2000–3000 K (see (4)) during the whole laser pulse. Indeed, Fig. 8 shows that at the threshold laser intensity
Fig. 8. The spectral temperature as a function of the laser energy for several CCl$_2$F$_2$ percentages (as in Fig. 6): 5% CCl$_2$F$_2$, collected 1 cm above the RF electrode (circles), 1% CCl$_2$F$_2$, collected 1 cm above the RF electrode (triangles) and 1% CCl$_2$F$_2$, collected 2.5 cm above the RF electrode (diamonds).

the particulate temperature is significantly lower (2700 K) than the "normal" decomposition temperature (3500 K). Both the laser-induced emission intensity and the temperature saturate at high laser intensities. The saturation temperatures are always close to 3500 K and independent of the conditions in which the particulates were grown. Obviously, this is the decomposition temperature of the cluster material.

From the last observation it follows that a laser with an extremely high intensity is not necessarily efficient in inducing an intense blackbody-like radiation from particulates. Contrarywise, too high an intensity causes a fast particulate destruction, which limits the duration of the emission, without increasing its intensity ($T = \text{const}$). This is in agreement with the experiments with a Q-switched laser (pulse duration $\sim$20 ns). Typically we have observed a 100–1000 times lower emission at the same laser energy. In this case the surface heating and destruction are extremely fast, but the irradiated intensity is limited due to the fact that the destruction process occurs at a constant temperature. Small particulates ($\alpha \sim \kappa^{-1}$) are destroyed immediately, while for larger particulates ($\alpha \gg \kappa^{-1}$) 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 particulate. After the laser pulse the remaining particulates will cool down by internal heat conduction within less than 1 $\mu$s. Therefore the upper limit for the duration of this event is 1 $\mu$s. In comparison with the emission from a 100 $\mu$s 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 long and the absorbed intensity should, after heating the particulates, only balance the radiative losses at a temperature just below 3500 K to prevent the particulate destruction.

V. CONCLUSION

Laser interaction with particulates formed in an Ar/CCl$_2$F$_2$ RF plasma results in intense white light emission. The time resolved spectra show blackbody like curves with temperatures varying between 3500 K at the start of the laser pulse and 2500 K in the extinction phase. The time evolution of the total intensity shows a maximum at about 30 $\mu$s after the onset of the laser pulse which agrees with the calculated heating time for a 1 $\mu$m particulate. A corresponding delay for the temperature cannot be observed due to an inhomogeneous particulate size distribution. The typical particulate temperature of about 3500 K has been found in all dusty plasmas studied.

The temperature and the emission intensity saturate with the laser intensity, which suggest particulate decomposition at this saturation temperature.

She has been working together with her husband, Winfred Stoffels, at the Department of Physics, Eindhoven University of Technology in Eindhoven, The Netherlands. Since 1991 she has been preparing her Ph.D. thesis. The research concerns an experimental and numerical study of the physics and chemistry of low pressure RF discharges. Her particular interest are: dusty plasmas, ion and radical chemistry in electronegative plasmas, fluid and particle in cell models. The study involves various plasma diagnostics, like microwave cavity method, optical and infrared spectroscopy, mass spectrometry and several laser techniques (photodetachment, laser-particulate interactions).

REFERENCES


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