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Criteria of Applicability of Laser Thomson Scattering Measurements of Electron Properties in Reactive Plasmas

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In order to extend the applicable range of laser Thomson scattering to chemically reactive plasmas, the method of approach was first classified, and criteria for applicability were established. As an example, these criteria were applied, experimentally and numerically, to the specific case of an inductively coupled plasma (ICP) in a CF_4 gas. Implications of the results and directions for further studies are discussed.

1. Introduction

After a decade of systematic development work, laser Thomson scattering has become an established and indispensable method for studying electron properties [electron density and electron temperature, or more generally electron energy distribution function (eedf)] in glow discharge plasmas in inert gases having electron density in the range of 10^{15}-10^{20} m^{-3} 1). Glow discharge plasmas are not only operated in inert gases, but also in other gases, for example in materials processing such as etching and deposition and in light sources such as lighting and excimer lasers. These are usually called reactive plasmas. Because electrons play crucial roles for excitation/dissociation/ionization/attachment in reactive plasmas, it is natural to try to apply laser Thomson scattering also to this area. However, several anomalous effects have been experienced during these measurements, such as nonlinear increase of signal intensities against laser powers in a CH_4 plasma and an increase in plasma background radiation by laser injection into an XeCl excimer laser discharge. These anomalous effects suggest that the laser irradiation for the laser Thomson scattering measurement into reactive plasmas may perturb the plasma condition, thus invalidating the measurements. Therefore, it is important to establish general criteria for applicability of laser Thomson scattering to reactive plasmas. If such criteria are established, we know the discharge conditions to which this very useful technique can be applied with confidence, and for which we may be able to extract useful information for these plasmas.

It is the purpose of this article first to discuss the method of approach for this problem, discussed in Section 2, and then, as an example, to apply this method to an inductively coupled plasma (ICP) in a CF_4 gas which is shown in Section 3. Section 4 shows the direction for future studies.

2. Laser effects in plasmas in general

Laser photons induce various photo-reaction processes. In order to discuss about laser effects in plasmas in general, it is useful to classify these into two different kinds, from the

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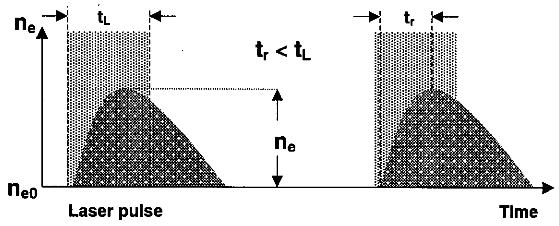

Fig. 1 The laser peturbation in case of an instantaneous effect. t_L is the laser pulse width and t_r is the rise time of n_e due to the laser irradiation. If $\Delta n_e/n_{e0} > 0.1$, the measurement becomes unreliable.

viewpoint of laser Thomson scattering of plasmas, as "instantaneous effects" and "accumulated effects", as follows.

2.1 Instantaneous effects

This case corresponds to the situation shown in **Fig. 1**, where photo-reaction processes produce appreciable changes in electron density during a single laser pulse. In order to check the presence of this instantaneous effect, a useful criterion is to do the following two experiments, and see whether the measured electron properties are the same.

(i) Dependence of laser photon energy, E_p ($h\nu$ dependence)

(ii) Dependence of laser pulse energy, E_L (E_L dependence)

In particular, we see whether the electron density is unaffected by these changes. However, the absence of any change in electron properties is only a necessary condition, not a sufficient condition, for the absence of laser induced effects, because the laser effects may have saturated already at the smallest laser energy or at the longest laser wavelength.

In order to study this case more vigorously, the following procedure can be followed. Firstly, (1) the types of particles that might exist in the plasma are listed, and next (2) the ionization energies of excited and ground states for each particle listed by step (1) are found. Finally, (3) the population density of each particle is estimated for these plasma conditions. This information is used to estimate the extra electrons that could be produced by photo-ionization of each particle type.

The measurement accuracy of laser Thomson scattering is about 10% , and so we would conclude a laser induced ionization reaction to be significant if the density of laserinduced additional electrons is greater than 10% of the measured density.

2.2 Accumulated effects

There can be cases where a single laser pulse does not produce appreciable extra electrons (not more than 10% of n_{e0}) as was described above, but accumulation of small effects of the plasma due to the laser irradiation may eventually lead to changes in electron properties. This is because the present Thomson scattering measurement relies on data accumulation of more than a few thousands shots. The small plasma change during a single laser shot may not only be from electron production but other photo-induced reactions, such as dissociation. This situation is schematically shown in **Fig. 2**.

2.2.1 Plasma residence time and laser repetition interval

One straightforward criterion to judge that this accumulation effect is not present for a certain discharge is to see whether the gas flow of the laser perturbed portion during two successive laser shots is smaller or larger than the diffusion length of the laser perturbed portion. If the former is larger than the latter, we judge this accumulated effect to be absent. If it is smaller, we may try to make it larger by increasing the gas flow rate while keeping the pressure constant. If an increase in the gas flow rate cannot make the

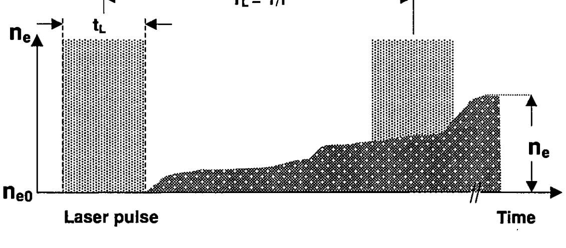

Fig. 2 The laser perturbation in case of an accumulation effect. Although a change in n_e during a single laser pulse t_L may be small, the accumulated change Δn_e after many laser shots may exceed 10% of n_{e0}.

former larger than the latter, then we have to think the next step for the judgement.

Figure 3 shows the plasma volume, and the ports for gas supply and pumping. From the figure or similar arrangements where the supplied gases more or less pass through the plasma volume, we see that the residence time (τ) of gas in the chamber is given by the following equation:

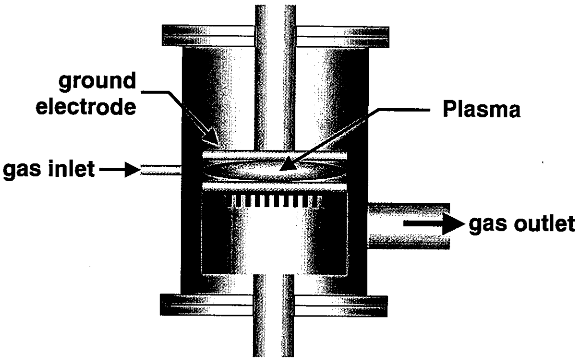

Fig. 3 Arrangement of the plasma volume, and the ports for gas supply and pumping.

$$\tau = V/P_s \qquad (1)$$
$$= pV/pP_s \qquad (2)$$
$$= pV/Q \qquad (3)$$

where V = volume of the chamber or plasma (litre)
P_s = pumping speed (litre/s)
p = pressure (Torr)
$Q = pP_s$: flow rate (sccm)
*79 sccm is 1 Torr-liter/s
or equivalent with 2.12×10^{21} particle/min (at 273 °K)

The accumulated effect is absent when $\tau < T_L = 1/f$, where f is the laser pulse frequency. It is to be noted that if particle diffusion becomes large during the time of 1/f, it may have to be taken into account.

2.2.2 Simulation of plasma relaxation time

Another approach is to use a discharge simulation, in which we try to observe the relaxation time τ_R after a given sudden parameter change of the discharge. If τ_R is smaller than $T_L = 1/f$, the laser perturbation decays away during the interval of two successive laser shots, and the effect cannot accumulate.

Because simulations are based on various assumption, we want to have experimental verification of the presence or absence of the laser accumulation effects. For this purpose, the above two experiments (i) and (ii) in Section 2.1 may also be useful. If electron properties deduced from Thomson scattering experiments using different laser photon energies and/or different laser pulse energies are different, it clearly indicates that the laser accumulation effects are present. In this case, we have first to distinguish whatever the effects are due to instantaneous effects or accumulated effects. The absences of the laser photon energy/pulse energy dependence, however, do not exclude the possibility of the laser accumulated effects, because, as in Section 2.1, the laser effects may have already saturated at the longest laser wavelength or the smallest laser energy. Under such circumstances, consideration similar to the last part of Section 2.1 has also to be followed when discussing accumulated effects.

3. Considerations for a specific case

In this section, the criteria described in Section 2 are applied to a low pressure ICP discharge operated in CF_4 gas, which is widely used for plasma etching of semiconductors. The results of the various tests can be used to judge the suitability of Thomson scattering for measurements in this specific plasma.

3.1 Effects of different laser photon energy and laser pulse energy

In Section 2, for both the instantaneous and accumulated effects, experiments to see the effects of different laser photon energy and laser pulse energy were shown to be useful. These

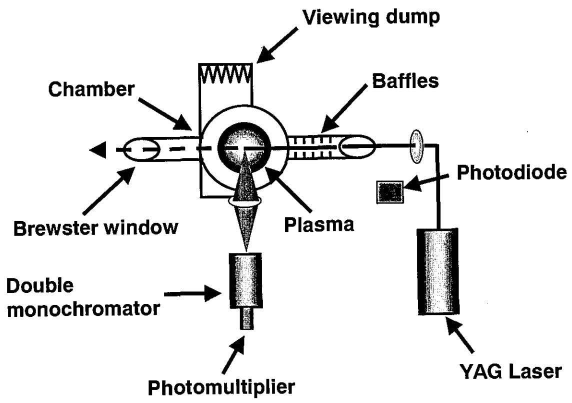

Fig. 4 Experimental arrangement for laser Thomson scattering using an infrared laser on an ICP discharge.

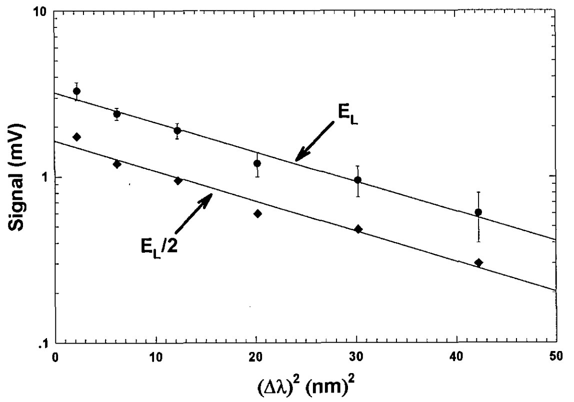

Fig. 5 Thomson scattering spectra, obtained at the wavelength of SHG (0.53 μm) at the full power of $E_L = 600$ mJ and half of this value of $E_L/2 = 300$ mJ.

Table 1 Measured electron properties by laser Thomson scattering using infrared and visible lasers.

Apparatus	Te. (eV)	n_e ($\times 10^{17}$ m^{-3})
1064nm	3.1±0.4	6.8±0.7
532nm	2.9±0.4	7.3±0.2

Table 2 Measured electron properties by laser Thomson scattering using the full laser power of $E_L = 600$ mJ and half the value of $E_L/2 = 300$ mJ.

Apparatus	Te (eV)	n_e ($\times 10^{17}$ m^{-3})
600mJ	3.1±0.4	6.8±0.7
300mJ	3.2±0.5	7.3±0.7

experiments were performed first.

(i) Dependence of laser photon energy, E_p ($h\nu$ dependence)

In order to perform this experiment, we developed an infrared laser Thomson scattering system[2], in which Thomson scattering signals from the fundamental wavelength of the YAG laser (1.06 μm) were detected using a sensitive infrared photomultiplier. The experimental arrangement onto an ICP discharge is shown in **Fig. 4**. Details of the discharge chamber are described in Ref. 3 and the laser Thomson scattering system in Ref. 2. The result obtained from this experiment is shown in **Table 1**, together with that from the usual second harmonic generated (SHG) laser output (0.53 μm) of the YAG laser. The results indicate that electron properties obtained by the two different wavelengths agree within experimental errors.

(ii) Dependence of laser pulse energy, E_L (E_L dependence)

The laser Thomson scattering experiments were carried out at the wavelength of SHG (0.53 μm) at its full laser energy of $E_L = 600$ mJ and half of this value of $E_L/2 = 300$ mJ. The results are shown in **Fig. 5** and the electron temperatures and densities deduced from **Fig. 5** are summarized in **Table 2**. The results indicate that electron properties obtained by the two laser energies agree within experimental errors.

(iii) Discussion

It can be seen from these results that no laser perturbation was observed. However, as already stated in Section 2, there is a possibility that the laser perturbation effect is already saturated at the lowest laser energy. In order to check this point, the number of electrons that could be produced by photon-ionization was estimated and compared with that originally existing in the plasma. This comparison was done for the processes shown in (1) — (3) in Section 2.

For the step (1), we list Ar, C, F, F_2, CF, CF_2, CF_3, CF_4, C_2F_4, C_2F_6, C^+, CF^+, $CF_2{}^+$, $CF_3{}^+$ and $CF_4{}^+$ as possible particles to exist in the CF_4 plasma. For the steps (2) and (3), it is not possible to draw an accurate diagram in the (energy-density) coordinate space as was performed for a hydrogen plasma[4]. This is partly due to the lack of sufficient data of ionization energies for the above particles, and also partly due to the lack of enough experimental analysis of plasma emission data from the CF_4 plasma as was performed for the hydrogen plasma[4]. Therefore, a rough estimate was made here, using a simple zero dimensional (no spatial distribution being considered) time-dependent numerical simulation.

In the plasma, many complicated physical and chemical reactions can occur, and in the present simulations, 37 dominant reactions were taken into account. These are 15 electron impact reactions, 12 inter-molecular reactions, and 10 reactions occurring at the chamber walls. Numerical calculations were carried out by solving time-dependent rate equations for these 37 reactions for the given electron density of 7×10^{17} m^{-3} and electron temperature of 5 eV. First, appropriate initial values were assumed for various species and the rate equations were solved until densities became stable (equilibrium state).

For the discharge conditions shown in **Fig. 5** and **Tables 1** and **2**, the following order of magnitude estimates were made: Ar (10^{21} m^{-3}), F (10^{20} m^{-3}), CF (10^{19} m^{-3}), F_2, C, C_2F_6 and CF_2 (10^{19} m^{-3}), C_2F_3 and CF_3 (10^{19} m^{-3}). Because other species had much less densities than 10% of ne (7×10^{17} m^{-3}), these would not yield any observable laser effect, as discussed in Section 2.1. The lowest ionization energy of the above particles seems to be around 8 eV for CF. More than three photon ionization is necessary for a laser photon of 2.3 eV to ionize CF from its ground level. Although sufficient data do not exist for these multiple photo-ionization cross sections for CF, we believe produced electrons to be less than 10% of n_e, from the experience of estimation for a hydrogen plasma[4]. Analogous discussions apply to other species.

3.2 Accumulated effects

From the above discussion, it appears that the laser effects have not occurred during the laser Thomson scattering measurements of CF_4 plasmas. In order further to check this from viewpoint of accumulated laser effects, various quantities discussed in Section 2.2 were calculated.

(1) Residence time

The plasma volume was VP = 5 litres (plasma height of 75 mm and plasma diameter of 300 mm). Note, that the whole chamber volume was about 51 litres (720 mm height and 300 mm diameter), and but the presence of internal chamber parts, containing the rf coil and the ground electrode, make the effective volume of the chamber ~35 litres. We define the residence time in the plasma (τ_{plasma}) and in the chamber ($\tau_{chamber}$) using these volumes in Eq. (3).

Figure 6 shows τ_{plasma} and $\tau_{chamber}$ at a pressure of 20 mTorr. Also shown with a dotted line is $T_L = 1/f$, the time between two successive laser pulses operated at f = 10 Hz.

As an example, we take a typical operating condition of Section 3.2 of Q = 160 sccm (~ 2 Torr-litre/s), then **Fig. 6** yields $\tau_{plasma} = 50$ ms and $\tau_{chamber} = 350$ ms. Because τ_{plasma} is to be compared with T_L, we see that $\tau_{plasma} < T_L$, implying that any laser effect, even it occurred, must have disappeared before the arrival of the next laser pulse. Therefore, no accumulated plasma effect is anticipated, because the affected plasma volume is replaced well before an arrival of the next laser pulse.

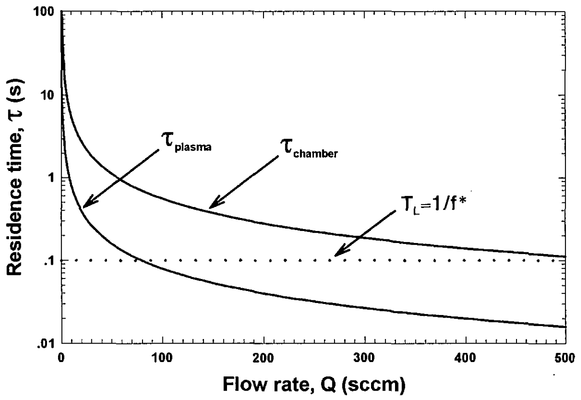

Fig. 6 The calculation of resident times τ_{Plasma} and $\tau_{Chamber}$ in [s] against Q, the gas flow rate in [sccm] at a pressure of 20 mTorr.

(2) Simulation of plasma relaxation time

The same numerical simulation as used in the discussion in Section 3.1 (iii) was performed. After a stable equilibrium state was reached, a sudden perturbation of 10% decrease in densities to seven dominant species (CF_4, CF_3, CF_2, CF, F_2, F^- and C_2F_6) were given, and recovery times to the above equilibrium state, τ_{rec}, were calculated.

$(\tau_{rec})_{max}$, namely the longest time among various recovery times for different perturbations, was found to be $(\tau_{rec})_{max} \sim 12$ ms. This is much smaller than T_L = 100 ms for the 10 Hz operation. Therefore, we conclude that the laser induced perturbation by a single laser pulse, if there is any, would die down well before the arrival of the next laser pulse.

4. Discussion: directions for the future

In the present paper, we first have formulated the method of approach to tackle the problem of the laser-induced perturbation during laser Thomson scattering measurements in reactive plasmas, and established criteria for applicability for a particular measurement. Then, we applied the criteria to a specific example of a CF_4 plasma, and showed experimentally and numerically that the laser induced perturbations do not occur for the particular discharge condition investigated. Based on this result, Thomson scattering measurement were performed to investigate the discharge properties eedfs at different discharge conditions were measured and interesting results were obtained[5].

It was evident from the result of a H_2/CH_4 plasma that a laser pulse can perturb the plasma state so that laser Thomson scattering is not applicable for certain discharge/laser conditions. Therefore, we next intend to carry out a detailed study of an Ar/O_2 plasma at various discharge conditions, gas flow rate and laser repetition frequency so that we hope to see transitions from no to appreciable laser effects. In this way, we hope to test the validity of the above established criteria more quantitatively.

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