Jpn. J. Appl. Phys. Vol. 36 (1997) pp. 134–138
Part 1, No. 1A, January 1997

Time Resolved Analysis of C_2 Emission from Laser Induced Graphite Plasma in Helium Atmosphere

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(Received May 2, 1996; accepted for publication July 8, 1996)

We report time resolved study of C_2 emission from laser produced carbon plasma in presence of ambient helium gas. The 1.06 μm radiation from a Nd:YAG laser was focused onto a graphite target where it produced a transient plasma. We observed double peak structure in the time profile of C_2 species. The twin peaks were observed only after a threshold laser fluence. It is proposed that the faster velocity component in the temporal profiles originates mainly due to recombination processes. The laser fluence and ambient gas dependence of the double peak intensity distribution is also reported.

KEYWORDS: laser ablation, plasma, carbon clusters, time resolved spectroscopy

1. Introduction

Laser ablated plasmas are currently a topic of considerable interest. Pulsed laser deposition is an effective method for the production of a variety of thin films with desired properties. Studies on pulsed laser ablation of graphite in helium gas atmosphere is considered to be one of the effective methods for the preparation of C_{60} and higher fullerenes.[1–3] By focusing a high power laser onto a solid target it is possible to get a high temperature and high density plasma. The plasma characteristics depend on the incident laser intensity, laser wavelength, pulse duration, pressure of the background gas etc.[4–6] Different spectroscopic techniques are used for the characterization of the ablated fragments in the laser induced plasma which include emission spectroscopy,[7–9] absorption spectroscopy[10,11] laser induced fluorescence,[12,13] resonance enhanced multiphoton ionization[14] and mass spectroscopy.[15,16]

In order to understand the processes leading to the carbon cluster formation and pulsed laser deposition, the mechanism of the plasma plume generation from the target material under laser irradiation and the interaction of the plume with the ambient medium in the plasma chamber should be studied in detail and this has been the subject of numerous experimental and theoretical investigations.[17–20] In spite of the large number of reports available in the literature, the studies on laser produced carbon plasma have not yet yielded a clear-cut picture on plasma dynamics of the cluster formation and such a situation arises mainly due to the complexity of the phenomena involved.[21,22]

In this paper we present some new results obtained from the time resolved spectroscopic analysis of the C_2 swan band emission from graphite plasma.

2. Experimental Setup

The experimental setup used for the present study has been described elsewhere.[5,23] The polycrystalline graphite target was mounted in a stainless steel vacuum chamber equipped with quartz windows such that the target surface could be irradiated at normal incidence using 1.06 μm radiation from a Q-switched Nd:YAG laser having pulse width of 9 ns and repetition rate 10 Hz. To avoid errors due to local heating and drilling, the sample was rotated about an axis parallel to the laser beam. The emission from the carbon plasma was viewed normal to its expansion direction and imaged using appropriate focusing lenses and apertures onto the slit of a scanning monochromator (Jarrel Ash, 0.5 m, resolution 0.025 nm) coupled to a photo multiplier tube (PMT, S20 cathode). The monochromator has a spectral response in the 300–900 nm wavelength region. For spatially resolved studies, different regions of the plasma plume were focused onto the monochromator slit. In our studies the accuracy in spatial position was better than 0.2 mm. The characteristic lines were selected using the monochromator and the PMT output was fed to a 200 MHz digital storage oscilloscope (Iwatsu model DS 8621) with 50 Ω termination to record the emission pulse shapes. This setup essentially provides delay as well as decay times for emission from constituent species at a specific point within the plasma and these are extremely important parameters related to the evolution of laser ablated materials in a direction normal to the target surface.

3. Results and Discussion

The time resolved studies of emission lines from various species were made from the oscilloscope traces which showed definite time delays for emission with respect to the laser pulse. It has been found that each emission line has a distinctly different temporal profile. Each temporal profile represents a complex convolution of different factors that governs the temporal history of the emitting species, its production mechanism and rate, its flight past the viewing region and its radiative and collisional decay rate. The typical temporal profiles for C_2 species (choosing $\lambda = 516.5$ nm corresponding to (0, 0) band of swan system $d^3\Pi_g \rightarrow a^3\Pi_u$) at a distance of 1 cm from the target for different laser fluences are given in Fig. 1 (helium pressure 0.5 Torr). The initial spike in the figure is due to scattering caused by the laser beam, and can be used as a time marker. The time evolution of the spectral emission obtained in the present work clearly reveals that the C_2 species ejected by the graphite target has a twin peak distribution. This interesting feature appeared only above a threshold laser fluence and it varies with the distance from the target (*e.g.* 27.2 J/cm^2 for 1 cm radial distance from the target). Below this threshold fluence, only single peak distribution is observed. Another signif-

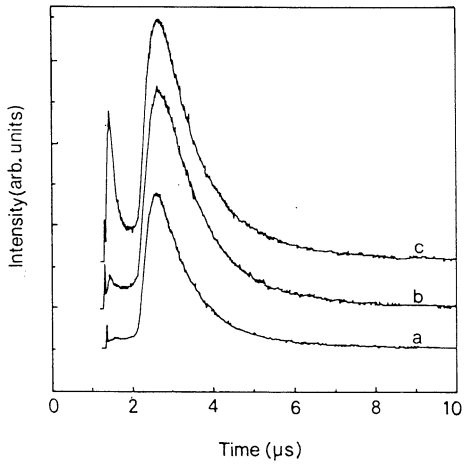

Fig. 1. Intensity variation of spectral emission with time for C_2 observed at 1 cm away from the target for laser fluences (a) 26.7 J/cm^2 (b) 27.4 J/cm^2 and (c) 28 J/cm^2 (helium pressure 0.5 Torr).

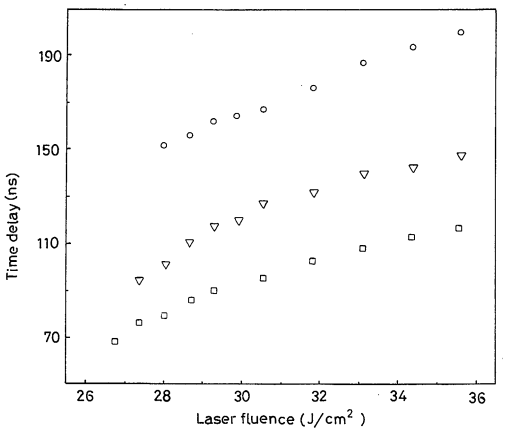

Fig. 2. Variation of time delays with laser fluence for the first peak at distances (□) 5 mm, (▽) 10 mm and (○) 15 mm (helium pressure 0.5 Torr).

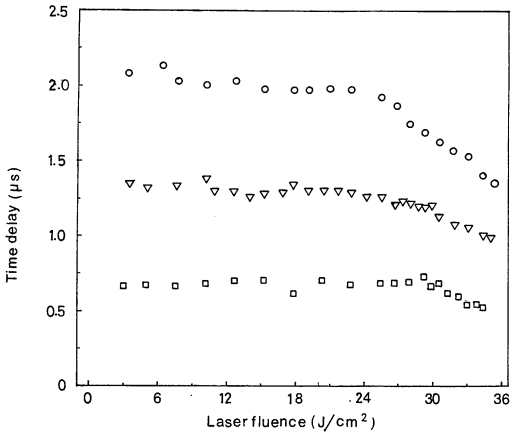

Fig. 3. Variation of time delays with laser fluence for the second peak at distances (□) 5 mm, (▽) 10 mm and (○) 15 mm (helium pressure 0.5 Torr).

icant observation is that the time delay of the first peak increases with laser fluence while that corresponding to second peak is constant up to a specific value of fluence and decreases thereafter. Also it is to be noted that the delay time for the first peak decreases with increasing ambient helium pressure, whereas the delay time corresponding to second peak has been found to increase with respect to helium pressure. Also the first peak gets narrowed while the second peak becomes broadened as the helium pressure is increased.

There are only a few reports available in the literature which describe twin peak time of flight (TOF) distribution in laser generated plasma from graphite target. Abhilasha *et al.*[24] reported a peculiar double peak structure in the temporal profile of C^+ species at 426.7 nm in a laser produced carbon plasma at various air pressures and they proposed that this may be due to stratification of the plasma into fast and slow ion components at the interface where the occurrence of Rayleigh-Taylor instability causes deceleration of the plasma front by ambient gas. A double peak distribution was also observed by Koren *et al.*[25] for C_2 species in polymide target and they attributed this to 'shell' (fast) and the 'core' (slow) emission components. Recently we reported[5] a twin peak structure for Y and YO emission in the laser produced plasma from $YBa_2Cu_3O_7$ and the twin peaks were assigned as due to species corresponding to those generated directly/in the vicinity of the target surface and to those generated from collisional and recombination processes.

At lower laser fluence, clusters of carbon along with electrons (by multiphoton/thermal process) are ejected from the target. Iida *et al.*[26] proposed dissociative mechanism for carbon particle formation at low energy density. At lower fluences it is expected that C_2 formation is mainly due to the dissociation of higher carbon clusters by collision processes with energetic electrons. The dominant mechanism for the production of C_2 band emission at low fluence is the electron collision with C_n cations ($n > 2$) and neutrals ($n > 2$) followed by dissociation and at higher laser fluences, Swan band emission is mainly due to the electron-ion, ion-ion recombination.[26]

Figures 2 and 3 show the variation of time delays with laser fluence in the case of first and second peak of C_2 respectively. The large mass of C_n will result in large time delays which are actually observed in the C_2 emission resulting in the occurrence of the delayed peak. Above the threshold laser fluence, the temperature of the plasma becomes so large as to dissociate C_n into neutral and ionized carbon atoms just outside the target. This will, therefore cause decrease in intensity of second peak above a certain value of fluence (Fig. 5). As laser fluence is increased, the enhancement in kinetic energy of C_2 molecule will reduce the time delay as observed from Fig. 3. Figure 4 gives variation of intensity of first peak with respect to laser fluence for different distances from the target showing saturation at higher laser fluence. The intensity of C_2 emission depends both on the spatial position from the target and on the delay time. For example dependence of the intensity on change in delay time brought about by spatial variation has been reported.[27]

Spectral analyses show that at low laser fluences, the emission spectrum is dominated by C_2 molecules whereas at higher laser irradiance the plasma emission is mainly

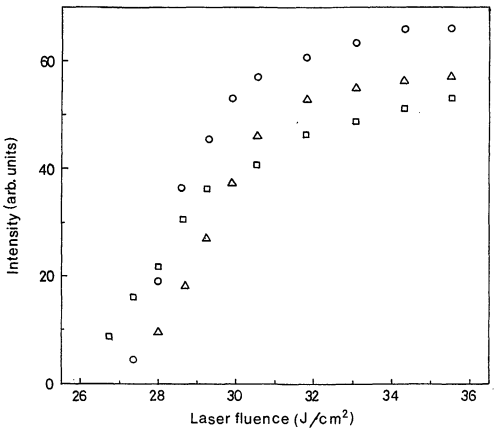

Fig. 4. Change in intensity for first peak with respect to laser fluence at different distances (□) 5 mm, (○) 10 mm and (△) 15 mm (pressure 0.5 Torr).

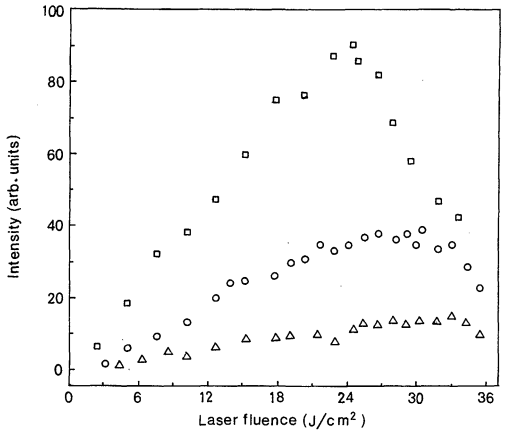

Fig. 5. Change in intensity for second peak with respect to laser fluence at different distances (□) 5 mm, (○) 10 mm and (△) 15 mm (pressure 0.5 Torr).

due to atomic and ionic species of carbon from CI to CIV. It is also observed that the ions have higher velocity as compared to neutrals and molecules because of the Coulomb fields which are generated by negatively charged electrons escaping from the plume. Above the threshold laser fluence, C_2 molecules are formed by radiative recombination of ions and electrons. This causes the occurrence of the first peak. The reason for the double peak formation can thus be attributed to the unequal delays caused from the different formation mechanism of C_2 in the plasma.

From Fig. 2, we can see that the time delay for the first peak increases with respect to increasing laser fluence which is contrary to the usual observation, where expansion velocity in the normal case increases with laser fluence. By considering the velocity distribution, this observation can be explained only if one can have some type of negative diffusion or anomalous diffusion of C_2 towards the target. Pappas *et al.*[28] observed the same phenomena for C_2 species using laser induced fluorescence detection technique and they explained it as due to selective depletion of high velocity C_2 species.

Once we have ions and electrons at higher laser fluence, they lead to production of carbon atoms by three body collision like

$$C^+ + e + e \rightarrow C + e \quad (1)$$

or collisional ionization *viz.*,

$$C + e \rightarrow C^+ + e + e \quad (2)$$

Near the target surface (2) may be more predominant than (1). As the laser fluence increases the number density of the plasma and the plasma temperature are also increased. This may cause large probability for events (1) and (2) to take place so that bulk of the C_2 may be formed at points nearer to the target surface only at later time on cooling of the plasma thereby causing more delay in the appearance of the first peak. In other words decrease in delay with laser fluence is superseded by increase in delay due to shift of major formation site of C_2 towards the target surface. This is further supported by the fact that the width of the first peak is visibly enhanced at higher laser fluences. Thus our studies show that C_2 species in the laser produced plasma from graphite consists of 2 types *viz.*, those generated due to dissociation of higher carbon clusters C_n ($n > 2$) (corresponding to slower peak) and those generated due to many body recombination processes which are predominant at higher laser. fluences (corresponding to faster peak).

In order to understand the mechanism more clearly, experiments were carried out by varying the helium gas pressure in the plasma chamber. Variation of time delay for the first and second peak with respect to helium ambient gas pressure is shown in Figs. 6 and 7 respectively. It is interesting to note that the delay for the first peak decreases and for the second peak it is increased with increasing helium pressure. The presence of helium gas helps cooling of plasma so as to reduce the plasma temperature. It is also supported by the fact that the increase of helium pressure decreases vibrational temperature of C_2 species.[29] The enhancement of delay time with the increase in gas pressure for the second peak in the temporal profile is, therefore, due to the reduction in the velocity of C_2 species. However, the time delay dependence on helium pressure corresponding to first peak cannot be explained easily as in the case of second peak. Decrease in time delay of the first peak with increase in pressure can be understood, at least qualitatively, as follows. Presence of helium gas reduces the plasma temperature so that the formation of bulk of C_2 through recombination process shifts towards the target surface. This reduction in time delay due to shift in formation site will exceed the enhancement in time delay due to reduction in velocity of C_2 species. This is in conformity with the observation of increase in delay with laser fluence.

Figure 8 gives the temporal profile of C_2 species for different helium ambient pressure. From Fig. 8, it is clear that with increasing pressure the first peak becomes more and more narrow with decreasing time delay, while the second one broadens with increasing time delay. The broadening of the second peak at higher helium pressures is mainly due to the enhancement in the collisional pro-

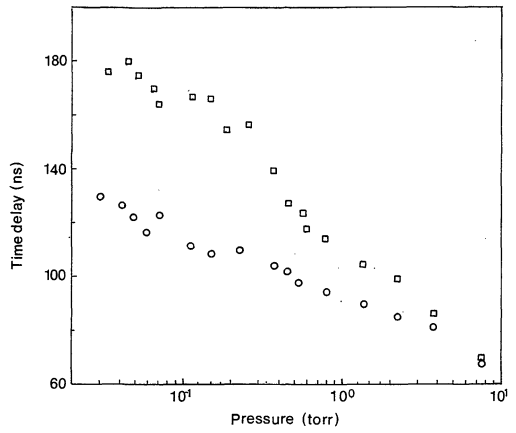

Fig. 6. Dependence of time delays of first peak on ambient helium pressure (○) 5 mm and (□) 8 mm (laser fluence 30 J/cm^2).

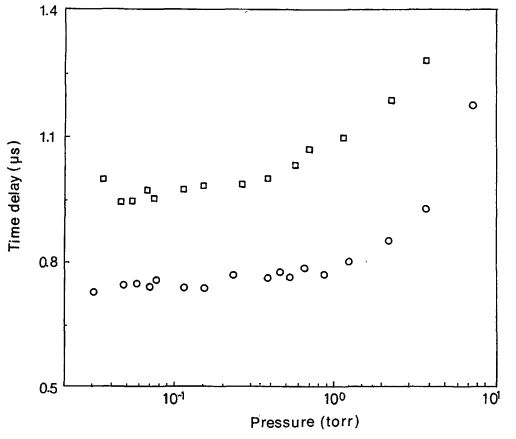

Fig. 7. Dependence of time delays of second peak on ambient helium pressure (○) 5 mm and (□) 8 mm (laser fluence 30 J/cm^2).

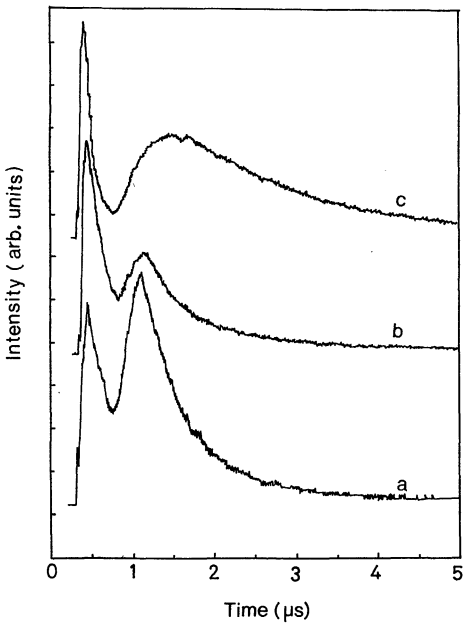

Fig. 8. Intensity variation of spectral emission with time for C_2 observed at 8 mm away from the target at different ambient helium pressures (laser fluence 30 J/cm^2) (a) 0.05 Torr, (b) 0.8 Torr and (c) 7.5 Torr.

cesses. Since we have assigned the second peak to the C_2 molecules formed by dissociation of higher clusters (C_n), the rotational and vibrational distributions in the excited state may not be related to the time of flight of these clusters. On the other hand the first peak which is formed due to recombination might reflect the effect of the initial kinetic velocity and type of recombination. Since there is an enhanced cooling effect at higher helium pressure we can expect a faster depletion of excited state population which will result in a narrower temporal profile for the first peak. This in fact is observed as seen in Fig. 8.

4. Conclusions

A graphite target was ablated by 1.06 μm radiation from a Q switched Nd:YAG laser in ambient helium atmosphere. Time resolved spectroscopic analysis of emission from C_2 species was carried out. The present work has differentiated the various mechanisms of the formation of C_2 species in the laser produced plasma from graphite in a helium gas atmosphere. We have observed a twin peak structure in the temporal profile of the emission lines from C_2 molecules above a certain threshold laser fluence. This is due to the delay caused from the different formation mechanism of C_2 in the plasma. These double peaks are assigned to formation of C_2 by recombination processes which occur only after a threshold laser fluence giving rise to first peak and through dissociation of higher carbon clusters by collision processes that are present at all laser fluences causing the second peak. The reduction of the plasma temperature due to cooling by the helium gas causes the sharpening of the first and broadening of the second peak with increasing helium pressure. Analysis of these data provides a fairly clear picture of the evolution and dynamics of C_2 species in the laser induced plasma from graphite and the role of carbon clusters in the same.

Acknowledgements

The present work is supported by the Department of Science and Technology, Government of India. One of the authors (SSH) is grateful to Council of Scientific and Industrial Research, New Delhi for a senior research fellowship. RCI and CVB are thankful to University Grants Commission, New Delhi for their research fellowships.

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