Expansion dynamics of laser ablated carbon plasma plume in helium ambient

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Received 11 September 2000; accepted 21 September 2000

Abstract

Time resolved emission spectroscopic measurements on a plasma plume generated by pulsed laser ablation of carbon in helium ambient atmosphere have been performed. Temporal profiles of electronically excited C\textsubscript{2} species show a twin peak distribution beyond a threshold laser irradiance. The emission features of C\textsubscript{2} species are found to be significantly influenced by the ambient helium atmosphere. It is observed that the helium ambient pressure and laser irradiance have opposite effects on the expansion dynamics of C\textsubscript{2} species. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 52.50.Jm; 52.25.Rv.; 52.70.Kz

Keywords: Laser produced plasma; Emission spectroscopy; Laser ablation; Plasma expansion

1. Introduction

Laser ablation of carbon has been extensively used for the deposition of diamond-like carbon (DLC) thin films and for the production of carbon clusters and nanotubes [1–3]. Carbon clusters like C\textsubscript{60} and higher fullerenes are well known to be formed as a product of laser ablation of carbon in an ambient helium atmosphere [4]. However, the underlying physics and chemistry of the processes such as carbon cluster formation or their dissociation are less than well understood. Several spectroscopic studies of carbon plasma have been carried out using a variety of laser wavelengths [5]. It has been shown that shorter wave-lengths are more effective for penetration into the sample, mainly because of large ablation rates possible at these wavelengths [6]. However, the main advantage in the use of near infrared (NIR) low energy photons is that, they are less likely to invoke photo-chemistry into the ablation phenomenon.

In the context of laser deposition of DLC films, it has been reported that high quality DLC films are obtained at moderate laser irradiances where molecular C\textsubscript{2} formation is prominent as revealed by its emission spectrum [7]. Laser ablation has the unique advantage that most of these molecules are formed in their excited states and hence spectroscopic measurements offer an excellent means to investigate their evolution and dynamics. Despite considerable experimental and theoretical progress, 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. In this paper, the emission features of laser ablated carbon plume generated in a helium ambient atmosphere are investigated using time resolved diagnostic technique. The effect of laser irradiance and helium ambient pressure on the expansion of electronically excited \( \text{C}_2 \) species in the laser ablated carbon plasma is discussed.

2. Experimental set up

The experimental set-up used for the present study is similar to the one described elsewhere [8]. The carbon plasma is generated by laser ablation of the high purity polycrystalline graphite sample using 1064 nm radiation pulses from a Q-switched Nd:YAG laser with repetition rate 10 Hz and pulse width 9 ns. The laser beam is focused normal to the target surface with an estimated spot size \( \approx 200 \) \( \mu \text{m} \). The target in the form of a disc is placed in an evacuated chamber provided with optical windows for laser irradiation and spectroscopic observation of the plasma produced from the target. The target is rotated to avoid nonuniform pitting of the target surface. The bright plasma emission is viewed through a side window at right angles to the plasma expansion direction. The section of the plasma is imaged onto the slit of a 1 m Spex monochromator using appropriate collimating and focusing lenses so as to have one to one correspondence with the sampled area of the plasma and the image. The monochromator is attached to a thermoelectrically cooled photomultiplier tube (PMT) for the light detection. For time resolved spectroscopic studies the output from the PMT is directly coupled to a 200 MHz digital storage oscilloscope with 50 \( \Omega \) termination. This set up essentially provides delay as well as decay times of emission from constituent species at a specific point within the plasma and 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 electron temperature \( (T_e) \) and density \( (n_e) \) of the carbon plasma are measured by the relative intensities of the successive ionization states of carbon atom and Stark broadening method, respectively. Dependence of these parameters on the distance from the target surface, delay time after the plasma initiation, and laser irradiance are discussed [9]. An initial temperature and density of about 3.6 eV and \( 3.5 \times 10^{17} \) \( \text{cm}^{-3} \) are observed and they decay rapidly to much lower values within 300 ns time. Electron density is inversely proportional to the distance from the sample surface \( (z) \) where as \( T_e \) decays \( z^{-0.1} \). Both \( n_e \) and \( T_e \) increased linearly, then reached a plateau at a laser irradiance of approximately 60 GW cm\(^{-2}\). The \( n_e \) and \( T_e \) are also found to be significantly influenced by ambient helium atmosphere [10].

Time resolved studies are carried out for emission from electronically excited \( \text{C}_2 \) species in the laser ablated carbon plasma. Time of flight (TOF) studies of the plasma give vital information regarding the time taken by a particular state of the constituent to evolve after the plasma is formed. This technique gives details on the velocity of the emitted particles and parameters which are of fundamental importance in establishing the mechanisms responsible for the particle emission [11,12]. Typical temporal distributions of \( \text{C}_2 \) species obtained by monitoring the spectral emission from \( \text{C}_2 \) in electronic excited state (at \( \lambda = 516.5 \) nm corresponding to the (0 0) transition of \( \text{C}_2 \) Swan system) recorded at a distance 5 mm from the target surface for different laser irradiances are given in Fig. 1. The time evolution of the spectral emission obtained in the present work clearly reveals that the temporal pattern of \( \text{C}_2 \) species ejected from carbon target has a twin peak distribution. This interesting feature becomes prominent only beyond a threshold laser irradiance and this threshold increases with increasing separation from the target surface. For example, at 5 mm from the target surface the twin peak structure is observed only beyond 74.3 GW cm\(^{-2}\). Below this threshold laser irradiance, only single peak distribution is observed.

The above observations indicate that the plasma apparently develops fast and slow components above a threshold laser irradiance. There exists a few reports that describe multiple peak distribution in the temporal profile in a laser produced plasma from carbon target. Laube and Voevodin [1] observed similar unusual velocity profiles when observed with a laser induced fluorescence optical emission spectrometer during pulsed laser deposition of DLC. Tasaka et al.
observed triple fold plume structure during Nd:YAG laser ablation of graphite into helium ambient atmosphere and during optical emission studies they found that the fastest component is composed of carbon ions, second fastest component is due to compressed neutral molecules and slowest component is due to radial vapor from the graphite target. Lowndes et al. [14] observed three modes of incident species in the TOF profile using ion probe method and they attributed it to scattered ions, ions that are slowed by gas phase collisions and slowly moving clusters formed through collisions, respectively.

There are two mechanisms that could exist for the particle formation during the laser ablation of carbon, viz. dissociative and recombinational [15]. It is expected that at low laser irradiance levels, graphite will be ablated layer by layer producing large particles. The dominant mechanism for the production of C₂ Swan band emission at low irradiances is the electron collision with Cₙ cations and neutrals (n > 2) followed by dissociation where one of the fragments is an ejected C₂ molecule. The dissociative mechanism can further be supported by the observation of long duration of Swan band emission at low irradiance levels [12]. As the laser irradiance is increased, the temperature of the plasma becomes so large so as to dissociate the Cₙ to neutral and ionized carbon atoms just outside the target. This is evidenced by the fact that we observe a rapid increase in the intensity of emission of ions with laser irradiance [11]. So at higher irradiance levels Swan band formation is mainly due to electron–ion and

Fig. 1. Intensity variation of spectral emission with time for C₂ species (516.5 nm) recorded at a distance 5 mm from the target for different irradiance levels: (a) 74.3 GW cm⁻²; (b) 77.8 GW cm⁻²; and (c) 81.4 GW cm⁻². For these measurements the helium pressure is kept at 0.05 mbar.

Fig. 2. Variation of time delay with laser irradiance for Pk1.
ion–ion recombination [15]. It is observed here that at high laser irradiances, after a threshold, an emission peak showing a faster component with higher kinetic energy for C$_2$ molecules begins to appear with a narrower temporal profile.

The variation of time delay with laser irradiance for faster peak (Pk1) and slower peak (Pk2) are given in Figs. 2 and 3, respectively. From these figures one can note that the delay of Pk1 increases with laser irradiance which is against the normal observation where velocity usually increases with the intensity of the incident laser pulse. Similar observations by one of the previous workers have been explained as due to selective depletion of high velocity C$_2$ species [16]. Contrary to the case of Pk1, delay of Pk2 remains almost constant up to a threshold laser irradiance (∼60 GW cm$^{-2}$) and thereafter it decreases.

The pressure of the ambient atmosphere is one of the controlling parameters of the plasma characteristics, as well as factors related to the laser energy absorption [10,17]. The presence of helium gas during the ablation process has dramatic consequences on the expansion dynamics. The temporal profiles are found to be very sensitive to the pressure of the background gas. With increasing pressure of the helium gas the temporal profile of Pk1 becomes more and more narrow, while for Pk2, it broadens (Fig. 4). It is also

Fig. 3. Variation of time delay with laser irradiance for Pk2.

Fig. 4. Temporal profiles of C$_2$ species at different ambient helium pressures: (a) 0.065 mbar; (b) 1 mbar; and (c) 10 mbar. These measurements are made at a distance of 8 mm from the target surface and at a laser irradiance of 81.34 GW cm$^{-2}$.
noted that the intensity of the Pk1 increases steadily with increase in helium pressure. But in the case of Pk2, the intensity is almost constant at low pressure regions, then it enhances. The helium serves to cool the hot electrons by collisions leading to a more efficient electron impact excitation and plasma recombination, leading also to the plasma confinement near to the target which enhances the emission from these species [18]. This is supported by the fact that electron temperature and density are found to be decreased with increasing helium pressure [10]. Variation of time delay for the peaks Pk1 and Pk2 with respect to helium ambient gas pressure is shown in Figs. 5 and 6, respectively. It is interesting to note that the delay

Fig. 5. Dependence of time delay of Pk1 on ambient helium pressures at different distances from the target surface.

Fig. 6. Dependence of time delay of Pk2 on ambient helium pressures at different distances from the target surface.
for the first peak decreases and for the second peak it is increased with increasing helium pressure, especially at high pressures.

The present results show that laser irradiance and pressure of the ambient helium gas have opposite effects on the plasma expansion processes. As irradiance increases, time delay for Pk1 increases while time delay for Pk2 is more or less constant up to a threshold irradiance and then decreases. Increase in helium gas pressure decreases the time delay for Pk1 and in the case of Pk2, time delay is being constant up to a particular pressure and then increases. Pressure and laser irradiance also showed opposite effects on narrowing and broadening of Pk1 and Pk2. With increasing irradiance, a broadening and narrowing phenomena is observed for Pk1 and Pk2, respectively. These interesting results can be explained by assuming a simple adiabatic model. Assuming adiabatic expansion model [19], the ablated material pushes the gas species until the plasma and gas pressures equilibriate. Then the length of the plasma \( L \) is given by

\[
L = A[(\gamma - 1)E]^{1/3\gamma}P_0^{-1/3\gamma}V_i^{(\gamma - 1)/3\gamma}
\]

where \( A \) is the geometric factor related to the shape of the laser spot at the target surface, \( \gamma \) the specific heat ratio \((C_p/C_v)\), \( E \) the laser energy density, \( P_0 \) the ambient gas pressure, \( V_i \) the initial volume of the plasma \( (V_i = v_0\tau_{laser}w) \), \( v_0 \) being the initial species velocity, \( \tau_{laser} \) the laser pulse duration and \( w \) the laser spot size at the target surface. The factor \( A \) depends on the expansion geometry and for a conical plume with a spherical tip and expansion angle \( \theta \) (for circular laser spot)

\[
A = \left(1 + \frac{1}{\tan \theta}\right)\left(\frac{3 \tan \theta}{\pi + 2 \pi \tan \theta}\right)^{1/3}
\]

From Eq. (1), it is clear that \( E/P_0 \) is the parameter controlling the length of the plasma if the experimental geometry remains constant; hence, \( E \) and \( P_0 \) should have opposite effects as experimentally observed in the present work. According to this model, the length of the plasma \( L \) is expected to increase as the laser energy density is increased or ambient gas pressure is decreased. Considering the experimental parameters used in this work, evaluating Eq. (1) with \( \theta = 35^\circ \) (then \( A = 1.6 \), \( \gamma = 1.66 \), \( v_0 = 5 \times 10^6 \) cm s\(^{-1}\), \( \tau_{laser} \approx 9 \) ns, gives approximately a straight line as shown in Fig. 7 corresponding to the present experimental pressure range. We have measured the plume length using time integrated photography which is also given in Fig. 7. The measured value of plume length fairly matches with the estimated value.

4. Conclusions

A radiation of 1064 nm from a Q-switched Nd:YAG laser is focused onto a carbon target where it produced
a transient and elongated plasma. Time resolved diagnostic technique has been used to characterize emission from electronically excited $\text{C}_2$ species. The present results show that the ambient gas pressure and laser irradiance have opposite effects on the temporal profiles of $\text{C}_2$ species. The broadening and narrowing of the multiple peaks with these parameters is expected due to collision and recombination phenomena. A simple adiabatic expansion model appears to provide a good description of the plume range and it is in reasonably good agreement with measured plume length using time integrated photography.

Acknowledgements

The author is thankful to Prof. H.J. Kunze, Prof. V.P.N. Nampoori and Prof. C.P.G. Vallabhan and Dr. C.V. Bindhu for their suggestions and support. Financial support from Alexander von Humboldt foundation (Germany) and Council of Scientific and Industrial Research (India) is gratefully acknowledged.

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