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Fine structure in the time of flight distribution of C_2 in laser produced plasma from graphite

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Abstract. Time resolved optical emission spectroscopy is employed to study the expansion dynamics of C_2 species in a graphite plasma produced during the Nd : YAG ablation. At low laser fluences a single peak distribution with low kinetic energy is observed. At higher fluences a twin peak distribution is found. It has been noted that these double peak time of flight distribution splits into a triple peak structure at distances $\geq$ 17 mm from the target surface. The reason for the occurrence of multiple peak is due to different formation mechanisms of C_2 species.

Keywords. Laser produced plasma; graphite; time resolved spectroscopy; carbon clusters; recombination.

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1. Introduction

In the past few years there has been growing interest in the laser ablation of graphite target since the first report on the existence of stable carbon clusters called Buckminster fullerenes [1–6]. It has been found that when graphite target is vapourized by intense laser pulses in a helium ambient atmosphere of moderate pressures, remarkably stable carbon clusters are produced. It is expected that fullerenes are formed when vaporized carbon condenses in an atmosphere of inert gas. Although considerable progress has a been achieved in studying carbon clusters (C_n) with $n \geq 10$, little effort has been spent for the characterization and production of low mass carbon clusters C_n with $n \leq 10$. Pulsed laser deposition is increasingly being utilized for thin film preparation, in which a laser beam is focused onto the target and the resulting vapor is made to condense on a substrate of interest [7]. Diamond-like carbon thin films (DLC) which are successfully prepared using laser ablation of graphite target have wide applications owing to their interesting characteristics like extreme hardness, electrical insulation, optical transparency and high thermal conductivity [8, 9].

In order to understand the processes leading to carbon cluster formation and pulsed laser deposition, the mechanism of plasma generation under laser irradiation and the interaction of the plume with the ambient background in the plasma chamber should be investigated in detail and this has been the subject of many experimental and theoretical

investigations [10–16]. In spite of the large number of, reports available in literature, 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 phenomenon involved. In this paper we report a comprehensive study of spatially resolved emission from C_2 molecules using time resolved spectroscopy. The temporally and spatially resolved spectroscopic studies are helpful to optimize parameters of DLC film deposition and to correlate the carbon cluster dynamics. To the best of our knowledge this is the first report regarding the existence of a triple peak in the temporal history of C_2 species from laser produced graphite plasma using time resolved emission spectroscopy.

2. Experimental setup

The experimental setup for the present study has been described elsewhere [17, 18]. A Q-switched Nd : YAG laser with fundamental frequency (1.06 μm, pulse width 9 ns) with repetition frequency 10 Hz is focused on a graphite target using a convex lens ($f = 23$ mm). The target is placed in a chamber with quartz windows in which helium gas at a pressure of 100 mTorr is maintained. The apparent length of the plasma at these pressures is about 25 mm. To avoid errors due to local heating and drilling, the sample is rotated about an axis parallel to the laser beam. The emission from the laser produced carbon plasma is imaged to produce a 1:1 image at, the entrance slit of a high resolution 1 m Spex monochromator, using appropriate focusing and collimating lenses and apertures, allowing spatial resolution better than 0.2 mm. The monochromator is equipped with a Thorn EMI Photomultiplier tube (PMT, model KQB 9863, rise time < 2 ns), connected to a digital storage oscilloscope (Iwatsu, model DS 8621, maximum sampling rate 200 MHz) with 50 ohm termination. The oscilloscope is synchronized with laser pulse using an internal trigger from the laser. The time of flight (TOF) of C_2 emission is recorded by setting the monochromator so as to record the spectral emission at $\lambda = 516.5$ nm corresponding to the (0,0) band of the Swan system ($d^3\Pi_g \rightarrow a^3\Pi_u$). Studies are made for various laser fluences as well as by varying the spatial separation normal to the target surface.

3. Results and discussion

Time resolved studies of emission lines from C_2 species were made using oscilloscope traces. 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 point and its radiative and collisional decay rate. Time resolved emission from any species shows a definite time delay for emission with respect to the laser pulse. The time difference between the initiation of the plasma and the time taken by the species to reach a specific point inside the plasma is called time delay of that particular species. There are many reasons for the occurrence of time delay for emission from any species which includes time of flight (TOF) of the species, thermal processes leading to plasma from the target, diffusion of the species through electric field created by other charged species, recombination and/or dissociation of the species etc. For e.g., if

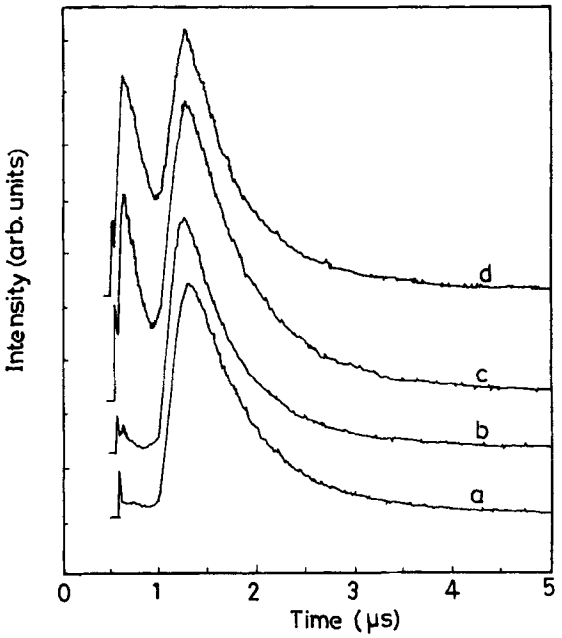

Figure 1. Intensity variation with time for 516.5 nm spectral emission from C_2 observed at 5 mm away from the target for laser fluences (**a**) 12.7 J cm^{-2} (**b**) 26.7 J cm^{-2}, (**c**) 28 J cm^{-2} and (**d**) 29.3 J cm^{-2}.

optical emission arises from electron impact excitation of species in the laser produced plasma, the excitation rate is proportional to the electron and species densities. Thus the time dependence of the emission intensity would be affected by the motion of electrons and that of the particles. Recently we reported spatial and temporal studies of C_2 species which reveal a double peak structure in time of flight (TOF) emission pattern beyond a threshold laser fluence [19]. Below this threshold laser fluence, only single peak TOF distribution is observed. The faster peak keeps on narrowing and the slower one becomes broadened with increasing helium pressure [20]. It is also noted that intensities of these peaks vary with laser fluence and helium gas pressure. The typical temporal profile for C_2 species (choosing $\lambda = 516.5$ nm corresponding to (0,0) band of Swan system at a distance 5 mm from the target for different laser fluences are given in figure 1. The initial spike in the figure is due to scattering caused by the laser beam, and can be used as a time marker. These double peak structure of C_2 species from carbon plasma were assigned due to species corresponding to those generated by dissociation of higher clusters which gives rise to slower velocity components, while those generated by many body recombination apparently gives rise to faster peak which are present only at higher laser fluences [19].

The present paper reports the observation of a triple peak structure in the temporal profile of C_2 species at distances ≥ 17 mm from the target surface. TOF spectra for C_2 species at various distances from the target is given in figure 2(a–f) for a laser fluence of 32 J/cm^2. For distances less than 17 mm from the target surface, there exist only a double peak structure in the TOF distribution (figures 2(a) and (b)). Thus, there exists a critical distance below which only double peak structure is observed while triple fold structure is

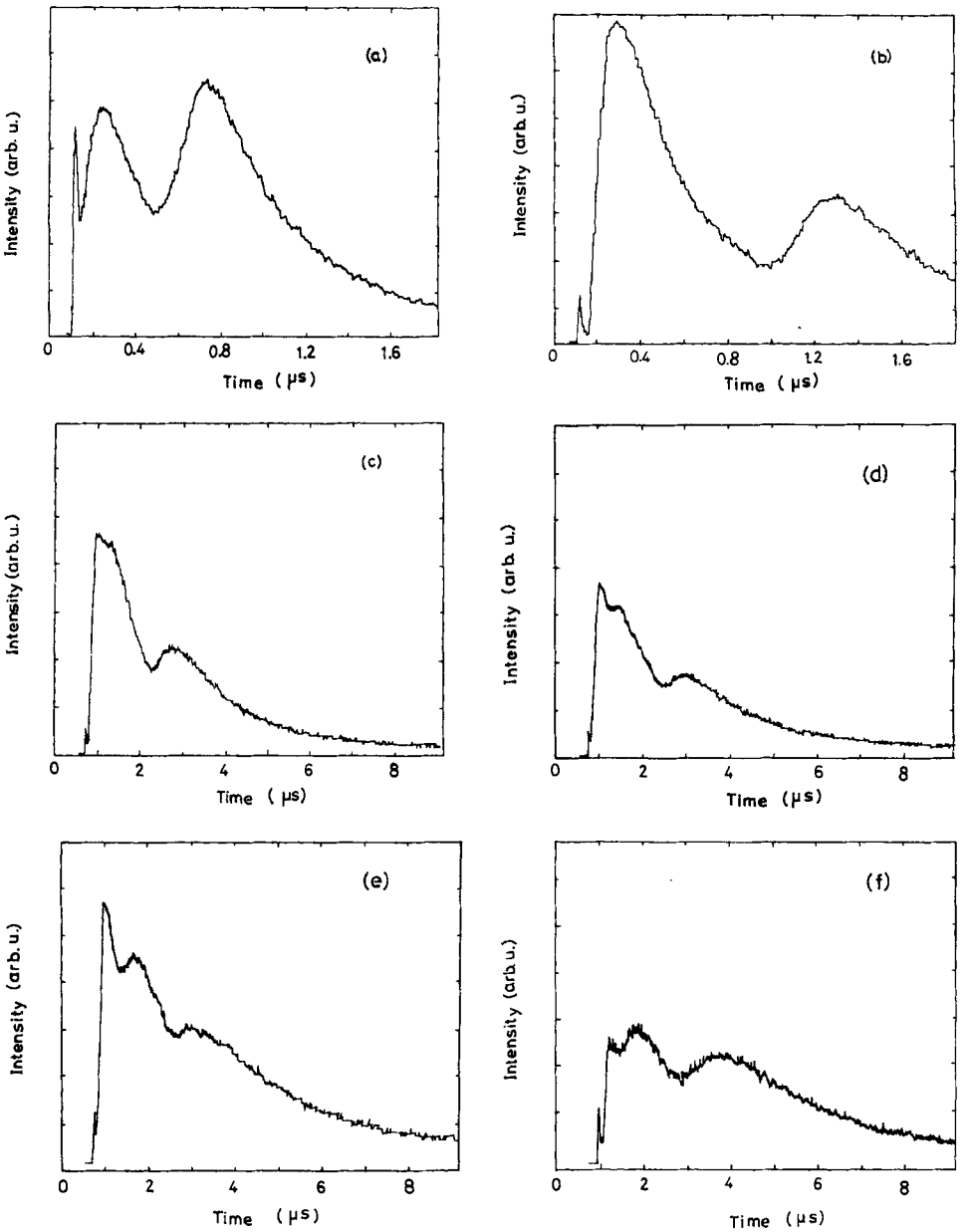

Figure 2. Intensity variation of spectral emission with time for C_2 species (516.5 nm) at different distances from the target. Distances are (**a**) 4 mm, (**b**) 10 mm, (**c**) 17 mm, (**d**) 18 mm, (**e**) 20 mm and (**f**) 22 mm. These TOF spectra are recorded at a laser fluence of 32 J/cm^2 and at a helium pressure of 100 mTorr.

observed beyond that critical distance. There are few reports which describe the triple fold time of flight (TOF) distribution in laser generated plasma from graphite target. Lowndes *et al* [21] recently observed three 'modes' of incident species in the TOF profile

using ion probe method and they attributed it to scatterd ions, ions that are slowed by gas phase collisions and slow moving clusters formed through collisions respectively. Tasaka *et al* [22, 23] observed triple fold plume structure during Nd : YAG laser ablation of graphite in helium ambient atmosphere and during optical emission studies using streak camera. They found that the fastest component is composed of carbon ions, second fastest component is due to compressed neutral molecules and the slowest component is the radial vapor from the graphite target. But the triple peak structure observed in these studies using time resolved spectroscopic technique is a highly spatial dependent one.

Two mechanisms exists for the C_2 formation, viz, dissociative and recombinational mechanisms. Most of the models of fullerene formation are based on the recombination mechanism, i.e., the formation by nucleation from carbon vapour consisting of carbon atoms and very small carbon molecules [24]. It is well known that graphite exhibits a large difference between the inter-layer and the intra-layer bond strengths. At low fluence, graphite will be ablated layer by layer producing large particles which in turn get dissociated to form C_2 species [25]. The dissociative mechanism can further be supported by the observation of long duration of Swan band emission at low fluences. At low laser fluences as in figure 1, only a slowly propagating component with low kinetic energy is observed. The larger masses of C_n will result in longer delays which are observed in the C_2 emission (dissociative mechanism) occurring at the lower fluences. The dominant mechanism for the production of C_2 Swan band emission at low fluences is the electron collision with C_n cations and neutrals ($n > 2$) followed by dissociation where one of the fragments is an ejected C_2 molecule [15]. As the laser fluence is increased, clusters with lower values of n will be ejected directly from the target. Above a threshold laser fluence, temperature of the plasma becomes so large so as to dissociate C_n to neutral and ionized carbon atoms just outside the target. During spectral analysis, we observed that at low fluence levels, the emission spectrum is dominated by C_2 molecules whereas at higher fluences the plasma emission is mainly due to ionic species of carbon up to C IV along with C_2 species. At higher fluence levels, Swan band formation is mainly due to electron–ion and ion–ion recombination. It is observed here that at high laser fluences, after a threshold, an emission peak showing a faster component with higher kinetic energy for C_2 molecules begins to appear. The observation of highly energetic peak at high laser fluences is attributed to the many body recombination of these carbon ions and electrons.

From the studies of ionic species it is found that the concentration of ionic species depend very much on the laser intensity. The expansion velocities of ionic species are found to be increased with increasing ionization. The expansion velocities calculated from the kinetic energy distribution of these ionic species are found to be maximum at 40 km/s, 58 km/s and 80 km/s for C II, C III and C IV respectively at a laser fluence of 32 J/cm^2. Hence most of the highly ionized atoms are located at the front of the expanding plasma which are followed later in time by species of lower stages of ionization. It is noted that the newly formed peaks have almost identical kinetic energy distributions in comparison with highly energetic ions. The observation of splitting of the recombinational peak at higher spatial distance is due to delays caused by different recombinational formation mechanism of C_2 species in the laser induced carbon plasma. The presence of helium ambient gas helps cooling of plasma so as to reduce the plasma temperature and confinement of the same, thereby increasing the recombination rate.

In conclusion, we have observed a triple peak structure in the time profile of C_2 species

in laser induced graphite plasma. We observed a double peaks, structure in the temporal profile at higher laser fluences and these double peak structure gets modified into triple peak distribution at distances $\geq$ 17 mm from the target. The cause of formation of these triple peak are assigned to the delay caused by different formation mechanism of C_2 species.

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