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CN emission spectroscopy study of carbon plasma in nitrogen environment ☆

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Abstract

Spectroscopic emission diagnostics of a carbon plasma created by an excimer KrF laser pulse at three laser fluences (12, 25 and 32 J/cm^2) is performed under nitrogen ambient at pressures of 0.5 and 1 mbar. By following the time evolution of the radical CN spectral emission profiles, we notice, at a certain distance from the target surface, the existence of twin peaks for the time of flight distribution. This double structure depends on laser fluence and gas pressure parameters. The first peak moves forward in relation with the plasma expansion whereas the second peak moves backward and it is attributed to CN species undergoing oscillations or reflected shocks.

Keywords: Laser ablation; Emission spectroscopy; Laser induced plasma spectroscopy

1. Introduction

Laser induced plasma spectroscopy is an effective tool to detect various transient species present in the above regions of the laser produced plasma from solid, liquid or gas. It is capable of performing measurement in any kind of matter [1]. In pulsed laser deposition, in presence of an inert or chemically active gas, the optical emission spectroscopy is widely used to diagnose the plasma plume [2–5], and it is suitable for performing the deposition process control. The solution of the processing control problem depends on the understanding of the basic physics and chemistry associated with laser-target and particle–particle interaction inside the laser induced plasma plume [6].

In the context of laser deposition of carbon nitride films CN_x, it is necessary to understand the formation and the dominance of the radical CN and their dependence on various parameters such as the laser fluence, gas pressure and laser wavelength. Some works on laser induced carbon plasma under nitrogen gas were performed in order to study the spatio-temporal evolution of the ablated species and the formation mechanism of molecular species such as C_2 and CN [7–10]. The results depend strongly on experimental parameters and the phenomena remain not completely understood.

Compared to the expansion into a vacuum, the interaction of the plasma plume with a reactive gas is a far more complex gas dynamics process due to the rise of many physical phenomena involved including deceleration, recombination, formation of shock waves and clustering. At intermediate ambient gas pressure, the ablated material and the ambient gas are compressed, and at a certain time the plume pressure equals the background gas pressure. As a result the plume pulsates backward [11]. The plasma reflection was already reported by Geohegan [12] using fast ICCD photography of graphite laser ablation into high-

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pressure argon. Also an oscillatory behavior of plasma induced by laser ablation of $YBa_2Cu_3O_{7-x}$ in oxygen and noble gases was revealed by Bulgakov and Bulgakova [13]. Their study was theoretically and experimentally made using a two-fluid gas dynamics model and time-of-flight mass spectrometry, respectively.

Our work is related to the characterization of graphite laser ablation in a nitrogen environment by emission spectroscopy at relatively high laser fluences. In the current paper we report the results obtained by analyzing the temporal profile of the radical CN as a function of distance from the target surface for two N_2 pressures, 0.5 and 1 mbar. Our experimental finding shows a double structure of the CN optical time of flight (TOF) spectra. The two components (slow and fast) evolve differently in time and in space. The study of the spatio-temporal evolution of the two components shows a moving back of the CN slow species, which were submitted to a reflection by the shock wave at the plasma front–gas interface.

2. Experimental setup

Carbon plasma was induced by a KrF excimer laser (Lambda Physik Compex102) operating at 248 nm with pulse duration of 25 ns and a repetition rate of 10 Hz delivering a maximum energy of 300 mJ per pulse. The laser beam was focused on a rotating graphite target at an incidence angle of 45° through a set of focusing optics. Two crossed 1 m focal length cylindrical lenses were aligned with a 0.5 m focal length spherical lens in order to obtain the smallest spot size ($0.66\ 10^{-2}$ cm^2) and then a relatively high laser fluence. The graphite target was mounted inside a stainless steel chamber evacuated to a pressure of 10^{-6} mbar and then filled with nitrogen gas at a pressure of 0.5 and 1 mbar. The plasma emission was optically imaged on a 100 μm entrance slit of Spex spectrometer with a magnification of 1 through a set of spherical and flat mirrors. Plasma emission was collected at right angle to the normal of the target surface from a region of dimensions 100 μm wide × 2 mm high fixed by the spectrometer entrance slit. The plasma image was horizontally translated at steps of 0.3 mm on the spectrometer entrance slit to provide spatially resolved measurements. A spectrometer containing a 1200 grooves/mm grating leading to a spectral resolution of 0.08 nm was coupled to a fast Hamamatsu R928 photomultiplier with a 2.2 ns rise time. This latter was connected to a digital oscilloscope (Tektronix TDS3032) with a 400 MHz band pass.

3. Results and discussion

The time integrated plasma emission spectra of laser ablated carbon in the presence of nitrogen at a pressure of 0.5 mbar were recorded and analyzed between 230 and 750 nm. The plasma emission spectrum is well dominated by CN molecular emission of Violet system ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) of the sequence ($\Delta v = 0, +1$), the C_2 emission of Swan system ($d^3\Pi_g \rightarrow a^3\Pi_\mu$) of the sequence ($\Delta v = 0, +1$), C^+, neutral carbon, N_2^+, N^+ and neutral atomic nitrogen. Peak wavelengths of the main lines and molecular bands of the emission spectra in nitrogen environment identified in this experiment are summarized in Table 1.

By following the temporal profiles of C, C^+ and N^+ lines at the respective wavelengths 247.8, 426.7 and 399.5 nm and the (0, 0) band head of CN, C_2 and N_2^+ at the respective wavelengths 388.3, 516.5 and 391.4 nm, we notice that the optical time of flight signal of C, C^+ and N^+ is made up by a single component with a delay time increasing with the increase of the observation distance from the target surface, while the optical time of flight signal of CN, C_2 and N_2^+ is made up by two components. The temporal profile of the emission of N_2^+ molecules is characterised by a prompt emission when the laser beam reaches the target surface, followed by a broad emission with time evolution similar to that of N^+ and C^+. This observation was already reported [14–16]. The prompt emission of N_2^+ could be due to the fast electron impact ionization and excitation of ambient nitrogen gas and the broad emission that comes from nitrogen molecules undergoing collisions in ionized vapour front.

The double structure of CN and C_2 time of flight is different from the N_2^+ one. The first component of CN and C_2 has a time delay which increases with the increasing of

Table 1
Peak wavelengths of the main lines and molecular bands of the emission spectra recorded during laser ablation

Atomic species	Wavelength (nm)	Excitation energy (eV)	Transition
CI	247.8	7.68	$^1S_0-{}^1P_1$
CII	274.7	20.84	$^2P-{}^2D$
CII	283.7	16.33	$^2S-{}^2P$
CII	407.6	27.4	$^4D-{}^4F$
CII	426.7	20.9	$^2D_{5/2}-{}^2F_{7/2}$
NII	399.5	21.5	$^1P_1-{}^1D_2$

Molecular species	Vibrational band	Wavelength (nm)	Excitation energy (eV)	Electronic transition
C_2 Swan system	(0–0)	516.52	2.4	$d^3\Pi_g \rightarrow a^3\Pi_\mu$
	(1–1)	512.93		
	(2–2)	509.77		
	(1–0)	473.71		
	(2–1)	471.52		
	(3–2)	469.76		
	(4–3)	468.48		
CN Violet system	(0–0)	388.34	3.2	$B^2\Sigma^+ \rightarrow X^2\Sigma^+$
	(1–1)	387.14		
	(2–2)	386.19		
	(3–3)	385.47		
	(4–4)	385.09		
	(1–0)	359.04		
	(2–1)	358.59		
	(3–2)	358.39		
N_2^+ First negative system	(0–0)	391.4	3.1	$B^2\Sigma_\mu \rightarrow X^2\Sigma_g^+$