TIME-RESOLVED SPECTROSCOPIC DIAGNOSTICS OF REACTIVE PULSED LASER PRODUCED PLASMAS DURING THIN FILM DEPOSITION

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Abstract

This paper presents diagnostic data obtained from the laser ablated plume of a composite graphite sample during carbonaceous films production. The major species including Cl, CII, and C₂, C₃ radicals within the plume have been identified. From emission spectrum of C₂ molecules the vibrational temperatures at various experimental conditions were determined. Based on the results of quantitative spectroscopic diagnostics the character of the evolution of plasma parameters and processes of formation of molecules and clusters were analyzed at various initial conditions of plasma creation. The characteristics of deposited material are also discussed.

1. Introduction

Laser-ablation plasmas are very attractive for numerous technological applications, in particular, for the deposition of thin carbonaceous films (diamond like carbon, polymer protective and cluster assembled coatings), carbon nanotube production [1-3]. Laser ablation of carbon containing targets results in formation of different carbonaceous structures depending on the conditions of laser ablation experiment, in particular on the incident laser fluence, environment atmosphere composition and pressure. The physical properties of plasma plume, such as species concentrations and temperature, directly affect the properties of the material being fabricated. In order to optimize the laser plasma based technologies the understanding the basic physical and chemical processes responsible for mechanisms of pulsed laser deposition is required.

The distinctive features of laser ablation plasmas are complex spatio-temporal structures and a wide range of varying of plasma parameters during the plasma existence time. In a study of such plasmas one has to combine of short time scales (ns), small spatial dimensions (~ 0.1 mm), consequently strong plasma density gradients and the low density of the active species. For obtaining the quantitative information on plasma parameters, like spatial and temporal evolution of transient species the currently available techniques should be adopted and laser aided diagnostics must be developed, which combine high sensitivity with a good spatial and temporal resolution.

In the present paper the time resolved spectroscopic studies of the laser-produced plasmas formed near the graphite composite samples has been performed. The laser-induced fluorescence method (LIF) combined with the time resolved emission spectroscopy was adopted to measure the spatial and temporal distributions of ions, atoms, and molecules in the laser ablation plume.
2. Technical details

The schematic diagram of experimental apparatus used in the present study is shown in Fig.1. Plasma was produced by focusing of a Nd:YAG laser radiation ($\lambda=1064$ nm, 10 ns FWHM, maximal energy 250 mJ/pulse), its second (532 nm, 150 mJ) or fourth (266 nm, 16 mJ) harmonics, and in some experiments of a XeCl (308 nm, 10 ns, $10^8-10^9$ W/cm$^2$) laser radiation on the surface of the rotating samples placed in the chamber with helium (krypton) atmosphere at pressures varying in the range $10^3$ - 500 Torr. The maximal intensity of about $10^{10}$ W/cm$^2$ was created in the focal spot on the target. The carbon composite target was prepared by compressing a high purity graphite with 1% nickel catalyst powder. The plasma chamber was evacuated to a pressure of less than $10^3$ Torr and then filled with helium (krypton) gas at desired pressures.

Optical observation of the plasma emission was performed by imaging the section of the plasma plume onto the entrance slit of monochromator equipped by the fast photomultiplier. The emission spectra of plasma were recorded in the UV and visible region (240 - 680 nm) at three different distances from the target surface (0.2, 1, and 3 mm). The maximal spectral resolution available was better than $3\cdot10^{-2}$ nm. The detection of the photomultiplier signals was accomplished by a transient digitizer, connected to a personal computer for data processing, storage and analysis. The experimental set-up allowed analyzing the evolution of the plume composition as a function of the distance from the target surface and time.

For LIF excitation the other available Nd:YAG laser was used to pump the Ti:sapphire laser tunable in the range of 690 - 1000 nm. The second harmonic of this laser (350 - 500 nm) was applied to excite the $(0,2)$ transitions of the $C_2$ Swan band between 435 and 438 nm. The $C_2$ fluorescence was detected in the $(2,1)$ band near 470 nm. This off-diagonal approach avoided scattered laser light and improved the signal-to-noise ratio. The fluorescence was collected for different time delays (0.25 to 50 $\mu$s) between the ablation laser and the probe laser as well as at different distances from the target. The use of crossed probing and viewing beams means that the requirement of local measurements has been satisfied.

![Fig. 1. Experimental set-up:](image)

1 - tunable Ti:sapphire laser, 2 - control unit, 3 - computer, 4 - Nd:YAG laser, 5 - digital oscilloscope, 6 - monochromator, 7 - photomultiplier, 8 - rotating carbon composite target.

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3. Results and discussion

The emission spectra (from 240 to 680 nm) are recorded at different locations from the target and at different pressures of an ambient gas. The intensities of the spectral lines were found to be dependent on experimental parameters. A typical emission spectrum of laser-produced plasma from the graphite target is shown in Fig.2.

The spectra were dominated by the C$_2$ Swan bands ($d^3\Pi_g - a^3\Pi_u$), appearing on a top of the continuous radiation in the long-wavelength part of the spectra. The recorded Swan bands included $\Delta \nu = +1$ (470-475 nm); $\Delta \nu = 0$ (510 - 516 nm); $\Delta \nu = -1$ (550-565 nm); and $\Delta \nu = -2$ (595 - 615 nm); where $\Delta \nu$ is the difference of the vibrational quantum numbers between the upper and the lower states of transition [4]. It should be noted that the presence of the Swan bands is typical for a laser-produced plume with conventional low-repetition-rate high pulse power laser ablation [5,6].

The emission spectra in the wavelength range 390 - 420 nm were identified as the C$_3$ (Comet Head System: $A^1\Pi_u$ - $X^1\Sigma_g^+$) and the C$_2$ Deslandres - d'Azambuja ($C^1\Pi_g$ - $A^1\Pi_u$) bands. The C$_2$ high-pressure bands in the spectra were also recorded including the (6 - 7) band at 543.4 nm and (6 - 8) band at 589.9 nm. The high-pressure bands are known to be part of the Swan system with $v' = 6$ levels excited at relatively high pressures [4].

Fig.2. The fragment of the emission spectrum of the carbon plume generated by laser ablation of graphite target in 400 Torr helium. The spectrum was obtained at distance of 0.2 mm from the target surface.

Together with the C$_2$ Swan bands, a radiation from atomic carbon Cl (248, 283, 477, 538 nm) and single-ionized CII (251, 515, 589, 685 nm) carbon ions was also detected. However there was no detectable Heli and KrI emissions.

The spectral intensities dropped off by a factor of 10 from location of 0.2 to 1 mm from the target. The particular nature of molecular band intensities at different distances results from
the fact that excited state formation is controlled by various interaction processes such as collisional excitation and ionization, recombination processes and fragmentation of higher molecular weight carbon species, which all vary greatly with the spatial separation from the target.

The emission characteristics of laser ablated plume were found to be also influenced by the pressure of the surrounding gas atmosphere. The increase in pressure leads to enhancement in the emission intensity from all the species due to the spatial confinement of plasma and more effective intraplume collisions. Besides, higher pressures resulted in production of greater amount of carbon ablation due to higher temperature surfaces at higher pressure.

The time evolutions of the plumes were obtained by transient measurements of emission at various wavelengths associated with peaks in the spectra. Time-resolved measurements of the laser-produced plasma emission showed that close to the laser pulse and up to 0.5 μs after it a strong and broad continuum radiation was emitted at all wavelengths. At later time the continuum radiation was greatly reduced and atomic and molecular line emissions are clearly seen above the continuum level. At these times in the plume expansion (close to the target while the plasma is sufficiently hot) the plume species are primarily electronically excited and the emission from excited states dominates the laser-induced fluorescence (from the ground states). It was also observed that in this period due to the high electron density the individual spectral lines of atomic and ionic emissions were highly Stark-broadened.

From temporal profiles of spectral lines obtained at different distances from the target the plasma expansion velocities were estimated. The expansion velocities varied with species, but in each case are typically ~10^4 ms^-1 at 10^9 W/cm^2 and decreased with decreasing laser intensity.

As the plasma expands, cools, and recombines, the ground states become populated, and LIF-emission emerges to compete with the spontaneous plasma emission. When the plasma emission completely disappeared, only LIF from ground states remained. According to previous measurements of clustering in laser plasmas expanding into background gas, this disappearance of the plasma emission usually signals the onset of nanoparticle formation [7].

It should be noted that in our experiments a continuum radiation above 600 nm became observable for the ambient gas pressure more than 400 Torr. This radiation may be attributed to a blackbody-like emission of particulate in the plume: of laser-heated particles ejected from the target at short delays (< 1μs) and/or of carbon aggregates formed in the plume at longer delay times (> 50 μs). Laser-induced blackbody radiation can be used to signal the presence of clusters and particles in the plume [8].

The intensities of the Swan vibrational bands were analyzed in order to determine the relative vibrational populations of the upper electronic state. The corresponding distribution of the molecules over the vibrational levels of a^3Π_u state was found to be nonequilibrium with predominant population of the upper vibrational levels. Such nature of the distribution was obtained from the intensities in the Δν = - 2, - 1, 0 sequences of the Swan system. The nonequilibrium vibrational population was observed both near the surface of the target (0.2 mm) and at the distance of 3 mm from it over the whole time during which the C_2 radiation was recorded. The nonequilibrium distribution is due to high-level states being overpopulated during C_2 formation process rather than by thermal excitation. Note that C_2 may be formed by recombination of carbon atoms or by photodissociation of larger carbon clusters. It is most likely that in our experiment at high (>10^9 W/cm^2) incident irradiance carbon dimers are formed predominantly through the recombination process. This hypothesis is additionally supported by the presence of the high-pressure bands in the C_2 spectra. The origin of these bands is most probably due to the population of the upper level of these bands via a potential-energy-curve
crossing by the metastable state which is populated preferentially during the formation of \( \text{C}_2 \) from free carbon atoms [9].

To get further insight we tried to characterize the main features of the vibrational population distribution by introducing some effective vibrational temperature for the groups of vibrational levels. Estimates of vibrational temperatures were made from the ratio of vibrational peaks in the spectrum and the Einstein spontaneous emission coefficients for the corresponding bands taken from [10]. In particular, we use the ratio of intensities of the vibrational peaks (1,0) and (0,0) of the \( \text{C}_2 \) Swan band. The estimated vibrational temperatures ranged from 17-10³ to 12-10³ K. These temperatures were calculated from time-integrated spectra and therefore represent time averaged values. Time-resolved measurements showed that at high laser fluences (10⁴ - 10¹⁰ W/cm²) molecular species in the laser ablated plume were formed when plasma temperature began to fall.

The increase of helium pressure increased the molecular band intensities and decreased the vibrational temperatures. Thus, addition of background gas is favor for cooling of the molecular species and increasing the recombination rate. The high vibrational temperatures of \( \text{C}_2 \) species estimated under various helium pressures indicate that the recombination of free carbon atoms is the most probable mechanism for the production of \( \text{C}_2 \) molecules in the plume. Thus, the dimer formation was likely a first step of clusterization of plume particles in the expanding plasma. Indeed, analysis of the material deposited from the plasma on the substrate using the adopted capillary electrophoresis method (by non-aqueous capillary electrophoresis with laser refractive index detection) showed the presence of carbon clusters in the fabricated products [11].

4 Conclusions

In conclusion, characterization of pulsed laser ablation carbon plasma by optical emission spectroscopy and laser induced fluorescence spectroscopy has been performed. The developed spectroscopic techniques were used to measure the spatial and a temporal distribution of constituents in pulsed laser ablation plasma expanding in the surrounding atmosphere. The developed diagnostics provided the required sensitivity and allowed improving the time and space resolution of measurements.

The major luminescence gaseous species including \( \text{C}_2 \) and \( \text{C}_3 \) radicals within the plume of laser ablated graphite composite samples have been identified. The spontaneous emission data reflects the excited state populations, which are mainly determined by the chemical processes that produce \( \text{C}_2 \) in the excited states (d³T₁g). In contrast, the ground state \( \text{C}_2 \) (a³Πu , 716 cm⁻¹), monitored by LIF may be in thermal equilibrium with its surroundings.

From emission spectrum of \( \text{C}_2 \) molecules the vibrational temperatures at various experimental conditions were determined. The vibrational temperatures were found to be much higher than the carbon sublimation temperature ( ~4100K for 100 Torr [12]). The time-space distributions as well as the vibrational temperature of \( \text{C}_2 \) molecules indicated that the dominant mechanism for production of \( \text{C}_2 \) was the atomic carbon recombination.

The results obtained can be useful in building a chemical model for carbon cluster formation during laser ablation of carbon containing samples in an ambient atmosphere. The presented spectroscopic analysis of the carbon vapor evolution in the ambient gas can be applied to a variety of cluster formation processes based on the laser ablation, such as production of carbon nanotubes and other carbon aggregated materials.
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References