

Optical Emission Studies of a Plume Produced by Laser Ablation of a Graphite Target in a Nitrogen Atmosphere

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Optical emission studies were performed to investigate thermal and dynamical properties of a plume produced by laser ablation of a graphite target in a nitrogen atmosphere. Experimental spectra of C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 1$) and CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\Delta v = 0$) were simulated to obtain the vibrational and rotational temperatures of the electronically excited species at various laser fluences and distances from the target. The spectroscopic temperatures of both molecules were found to be nearly independent of the laser fluence. The temperature of CN molecules was peaked in the middle of the plume while that of C_2 decreased with increase in the distance. At a given distance, the temperature of CN molecules was clearly higher than that of C_2 .

Key Words : Laser ablation, Optical emission spectroscopy

Introduction

Pulsed laser deposition (PLD) has been widely studied to grow a variety of carbon-containing refractory films such as diamond-like carbon,¹⁻³ carbon nitride,⁴⁻⁶ and silicon carbide.^{7,8} In particular, since the theoretical study of Liu and Cohen,⁹ extensive work has been done to deposit β -phase carbon nitride known as superhard material by laser ablation of a graphite target in a nitrogen atmosphere.

In PLD, the properties of the grown films are mostly affected by a laser-induced plasma, so called "plume" produced by irradiation of a target using a high power laser pulse. The plume consists of target materials, which are to be transferred to a substrate mounted facing the target. The composition of the plume is nearly identical to that of the target although there could be some mismatch due to an incongruent melting of the target and/or intentional supply of atoms from the ambient gas. For instance, inclusion of nitrogen atoms is achieved by supplying nitrogen via reactive laser ablation of a graphite target in a nitrogen atmosphere.

Not only such quantitative properties but also dynamical properties such as kinetic energy of each species in the plume have significant effects on the PLD-grown films. Also, vibrational and rotational temperatures of the molecules produced by chemical reactions in the plume are expected to be important parameters that determine the plume properties. In this respect, it would be important to elucidate the correlation between plasma parameters and deposited film properties,^{10,11} which is one of the ultimate goals of the research on the mechanisms of PLD.

Various analysis methods such as optical emission spectroscopy,¹⁰⁻¹⁷ time-of-flight mass spectroscopy,^{18,19} and laser-induced fluorescence^{20,21} have been adopted for the plasma diagnostics. Among these, optical emission spectroscopy is the most convenient and powerful technique because both qualitative and quantitative information can be obtained through analyses of the time- and space-resolved spectra:

concentrations, kinetic energies of the chemical species in the plume, and spectroscopic temperatures of molecules in their excited states.¹¹

In this work, we present experimental results on the laser ablation of a graphite target in nitrogen atmosphere and discuss the dynamics of plume expansion and formation of molecules by using optical emission and optical time-of-flight spectroscopy method. Optical emissions from the excited C_2 and CN molecules as well as atomic species, both ionic and neutral were observed and the vibrational and rotational temperatures of C_2 and CN molecules in their electronically excited states were derived via simulation of the spectra.

The evolution of the carbon plasma plume generated by laser ablation of a graphite target in an ambient gas is strongly dependent on the ablation conditions such as laser wavelength, fluence, ambient gas, and its pressure. In particular, temporal and spatial evolutions of C_2 and CN molecules in the plume were reported to be directly affected by the laser fluence, distance from the target, and ambient gas pressure.^{16,17,22-24} However, the expansion and formation mechanisms of C_2 and CN molecules are not fully understood yet and need further investigation.

Experimental Section

A schematic diagram of the experimental setup is depicted in Figure 1. A Q-switched Nd:YAG (Continuum Minilite II) laser at 1064 nm operating at 10 Hz was employed to ablate a graphite target whose diameter was 20 mm (Nilaco, 99.99%). The target was rotated during the experiment by a standard rotary motion feedthrough to reduce a target aging effect. The laser beam was focused with a lens of 25 cm focal length onto a target surface with an angle of incidence of 45°. The laser fluence on the target surface ranged from 1.3 to 3.1 J/cm² and the spot size of the focused laser beam was 1.1 mm². The graphite target was placed in a vacuum chamber that was evacuated to a base pressure of about

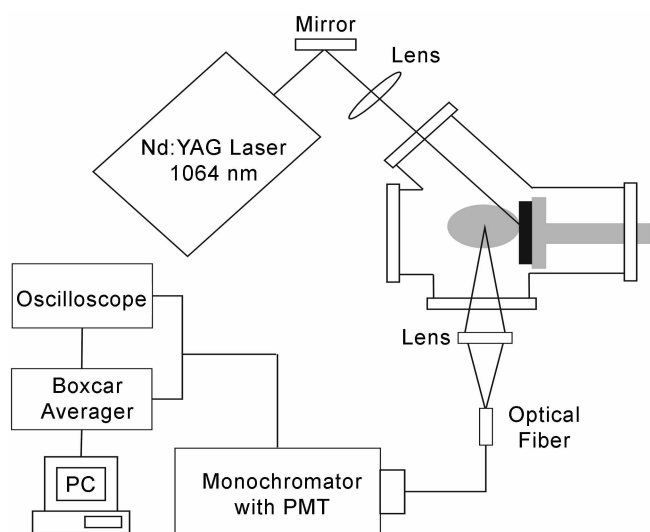


Figure 1. The schematic diagram of the experimental setup.

5×10^{-1} Torr. Nitrogen gas (99.999%) was fed to the chamber as an ambient gas, whose pressure was accurately controlled by a metering valve. During the laser ablation, the nitrogen pressure was varied from 100 mTorr to 50 Torr as measured by a vacuum gauge (Balzers PKR250).

Optical emission from the plume was collected, imaged onto an optical fiber (Spex 700FB) using a lens of 5 cm focal length, and ultimately sent to a monochromator coupled to a photomultiplier tube (Hamamatsu E1341). The photomultiplier signal was amplified and integrated by a boxcar averager (SR250). A storage oscilloscope (LeCroy 9361) was employed for temporal analyses of optical emission. For spatially resolved studies, sampling positions of the plasma plume were varied from 1.5 to 8.5 mm as measured from the target surface toward the direction of plume expansion.

Results and Discussion

A typical optical emission spectrum obtained by laser ablation of a graphite target in a nitrogen atmosphere is shown in Figure 2. In the spectral range of 350–575 nm, emissions from C_2 Swan band ($d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 2, 1, 0, -1$) and CN Violet band ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\Delta v = 1, 0, -1$) were dominant while ionic emissions from N_2^- (band head at 391.44 nm) and C^- (391.899, 426.7 nm) were just weakly observed at specific experimental conditions. The emission intensities were highly dependent on the ambient nitrogen pressures.¹¹

Figure 3 shows the variation of the emission intensities as the nitrogen pressure was increased from 100 mTorr to 50 Torr. The molecular emission intensities increased drastically with increase in the nitrogen pressure, while those of ionic lines decreased substantially at pressures above 10 Torr. It has been reported that the expansion of the plume is limited at high pressures and the plume is spatially confined.^{10,17} As a result, the dissociation rates of CN molecules overtake the formation rates at high pressures due to the increased number of energetic collisions in the plume.

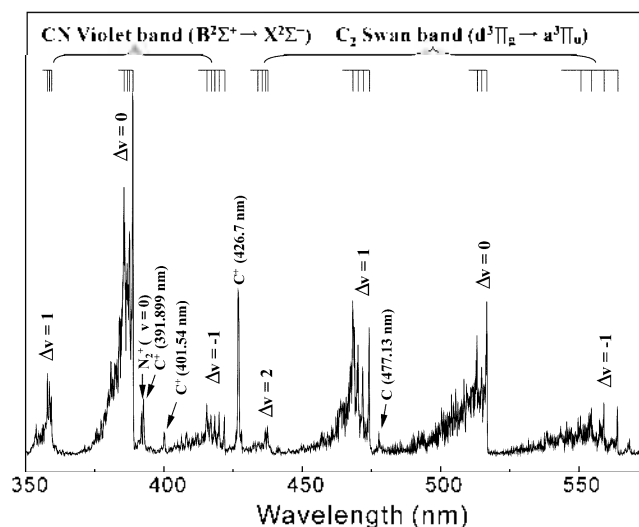


Figure 2. Typical optical emission spectrum of the plume generated by laser ablation of a graphite target in a nitrogen atmosphere measured at 4.5 mm. The laser fluence was 2.7 J/cm^2 and the pressure of N_2 was 10 Torr.

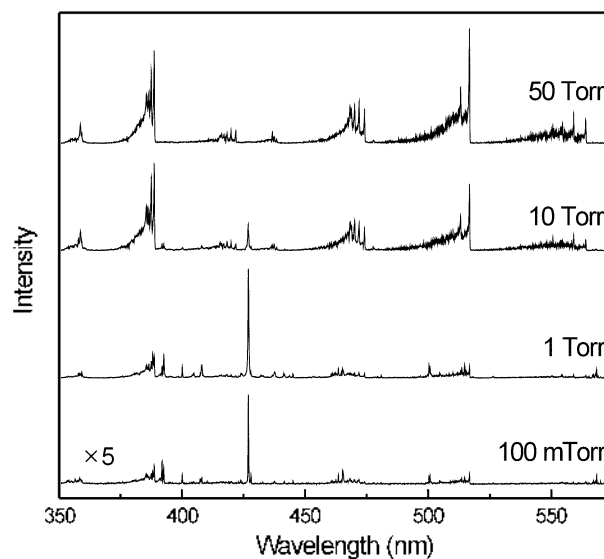


Figure 3. Optical emission spectra at various nitrogen pressures. The laser fluence was 2.7 J/cm^2 and the distance from the target was 4.5 mm.

The vibrational and rotational temperatures of C_2 ($\Delta v = 1$, 467–474 nm) and CN ($\Delta v = 0$, 385–388.4 nm) bands were obtained by simulation of the experimental spectra. Figure 4 shows the experimental and simulated spectra of C_2 ($\Delta v = 1$) and CN ($\Delta v = 0$) band with band heads at 473.7 nm and 388.3 nm, respectively. The spectroscopic constants used for simulation of the emission spectra were obtained from the previous works.^{25,26} The effects of laser fluence on the spectroscopic temperatures and emission intensities of C_2 and CN molecules are illustrated in Figure 5. With increase in the laser fluence, the number densities of the ablated species in the plume increased as expected. It is, however, surprising that the vibrational and rotational temperatures of C_2 and CN did not change noticeably by varying the laser

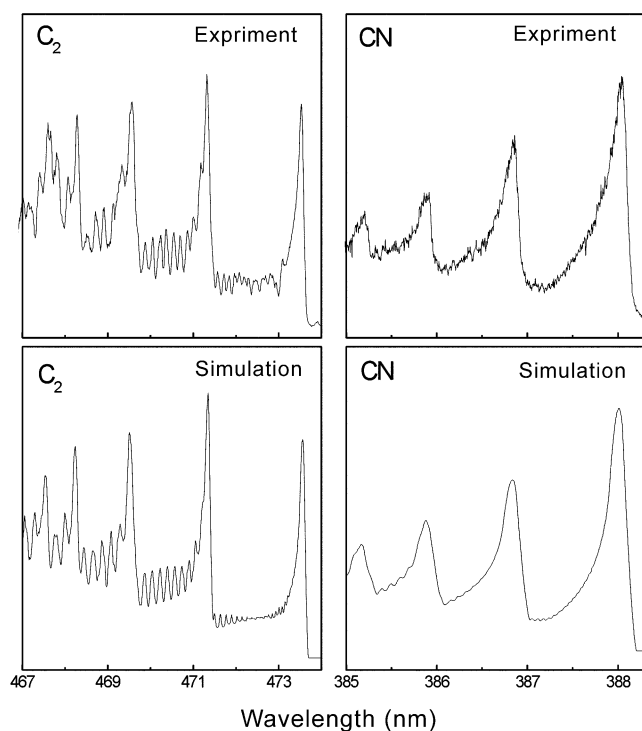


Figure 4. Comparison between the experimental and simulated spectra of C_2 ($d^1\Pi_g \rightarrow a^1\Pi_u$, $\Delta v = 1$) and CN ($B^2\Sigma^- \rightarrow X^2\Sigma^+$, $\Delta v = 0$) molecules. The laser fluence was 2.7 J/cm^2 and the pressure of N_2 was 10 Torr. The distance from the target was 4.5 mm.

fluence from 1.3 to 3.1 J/cm^2 . This does not conform to our previous result that was obtained in a similar experiment performed using the 4th harmonic (266 nm) of a Nd:YAG laser, where the spectroscopic temperatures of CN molecules, not C_2 , increased obviously with the laser fluence.¹³ We do not have clear explanation for the different result yet. We just guess that the formation mechanisms of CN molecules that affect the temperature are significantly dependent on the ablation wavelength.

It is certain that the vibrational temperature of C_2 molecules is higher than the rotational temperature over the fluence range in our experiment but, for CN, vice versa, even if we consider the maximum estimated error, 500 K, in deriving temperatures by simulation of the spectra. It is in general believed that CN molecules are formed by energetic collisions of C_2 and N_2 while C_2 molecules are mostly generated by the recombination of carbon atoms with no activation barrier in the gas phase.^{27,28} This explains why CN molecules are rotationally much hotter than C_2 as shown in Figure 5. Of course, C_2 molecules produced near the target, if any, at the early stage of plume formation may be hotter than CN.

The intensities and spectroscopic temperatures of C_2 and CN molecules as a function of the distance from the target are shown in Figure 6. The intensities of C_2 and CN show a similar behavior with distance, are peaked at around 4.5 mm, and diminish nearly to zero at distances farther than 7.5 mm away from the target, from which we can infer that the diameter of the plume is approximately 7.5 mm. Such behavior

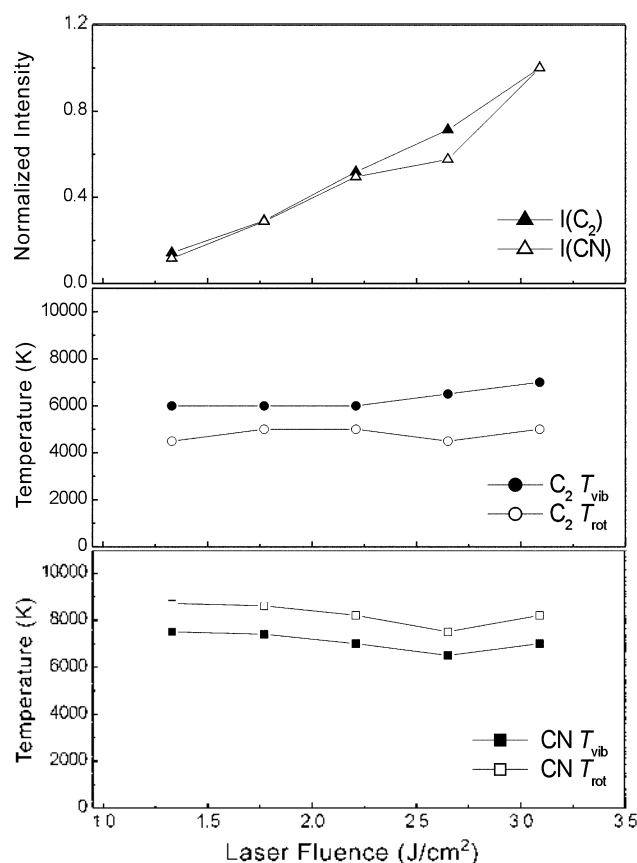


Figure 5. The normalized emission intensities, $I(C_2)$ and $I(CN)$, vibrational (T_{vib}) and rotational (T_{rot}) temperatures determined from the optical emission spectra of C_2 and CN molecules at different laser fluences. The pressure of N_2 was 10 Torr and the distance from the target was 4.5 mm.

with distance also supports the formation mechanism of CN mentioned above: C_2 molecules are precursors of CN molecules.^{11,27} At distances shorter than 2 mm, the vibronic populations in the electronically excited state of C_2 and CN molecules did not follow Boltzmann distribution. The temperature of C_2 molecules kept decreasing as the plume expanded because of the cooling effect.¹⁷ For CN molecules, however, the temperature gradually increased with distance, reached the maximum value at ~ 6 mm, and then decreased at farther distances. This implies that formation of CN molecules is most effective at the distance of ~ 6 mm where the energetic collisions are highly frequent.

We have examined the dynamics of ionic species by measuring the optical time-of-flight (OTOF) spectra of C^+ ions at 426.7 nm. Figure 7 displays the intensity of the OTOF spectra and peak arrival times at different distances. Unlike molecular species such as C_2 and CN, the intensity of the C^+ ions was peaked at the distance of ~ 3 mm and reduced to negligible magnitude after 4.5 mm, where the molecular species are enriched. The ionic species generated at an early stage of laser ablation are expected to be recombined with electrons near the target. The most probable velocity of C^+ ions as measured from the OTOF spectra was $\sim 1.3 \times 10^4 \text{ m/s}$, which is certainly higher than the

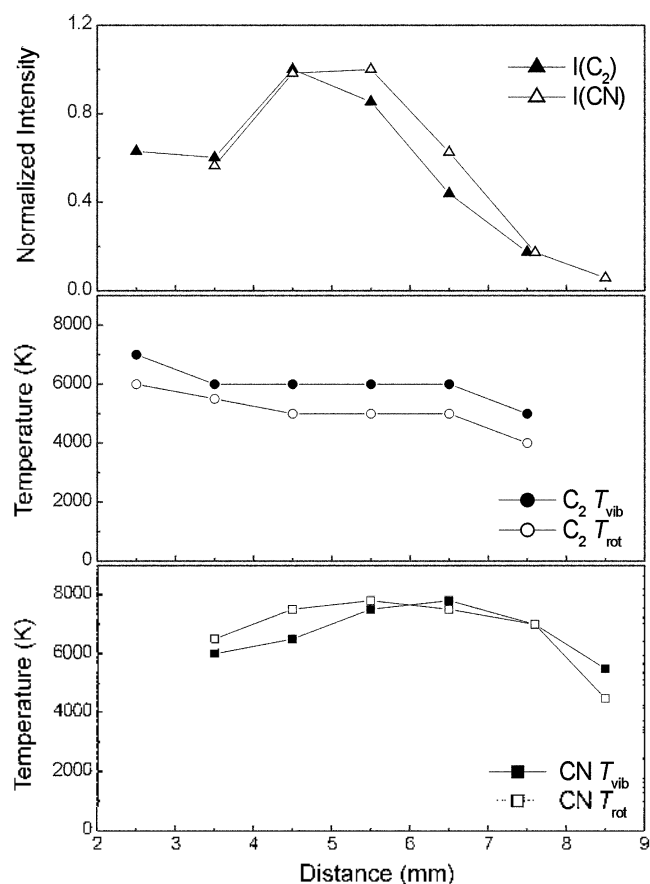


Figure 6. The normalized emission intensities, $I(C_2)$ and $I(CN)$, vibrational (T_{vib}) and rotational (T_{rot}) temperatures determined from the optical emission spectra of C_2 and CN molecules as a function of the distance from the target. The laser fluence was 2.7 J/cm^2 and the pressure of N_2 was 10 Torr.

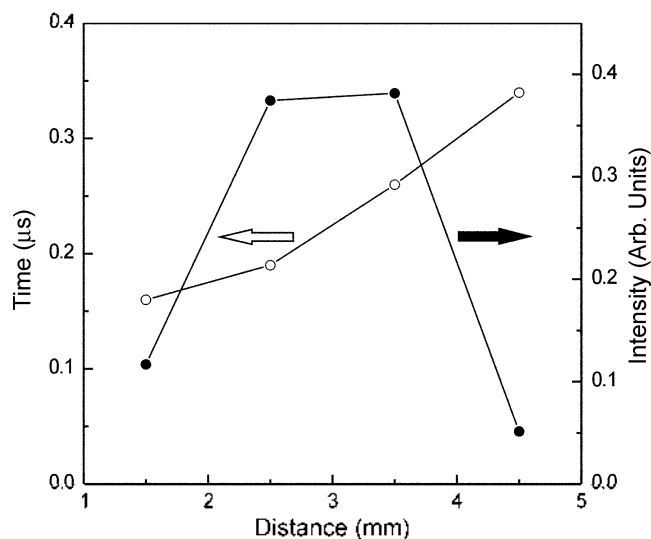


Figure 7. The emission intensity and peak arrival time of the C^+ (426.7 nm) ions as a function of the distance from the target. The laser fluence was 2.7 J/cm^2 and the pressure of N_2 was 10 Torr.

thermal velocity of molecules in the plume under the approximation of thermal equilibrium. Since the ions can be

accelerated under a temporal and local electric field in the plume, they are usually faster than neutrals.²⁹

Conclusions

We employed optical emission spectroscopy method to investigate the chemical species generated by laser ablation of a graphite target in a nitrogen atmosphere. C_2 and CN molecules were the dominant sources of optical emission at pressures above 10 Torr. At low pressures below 1 Torr, C^- was the most enriched species in the plume. Spectroscopic temperatures of the electronically excited C_2 and CN molecules were obtained by simulation of the experimental spectra. CN molecules were hotter than C_2 molecules presumably due to the differences in their formation mechanisms: C_2 molecules are formed by a recombination of carbon atoms while CN molecules are produced through a chemical reaction between C_2 and N_2 .

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