Effects of Transverse Magnetic Field on Laser-produced Carbon Plasma Plume in Nitrogen Atmosphere

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By adopting a time-resolved optical emission spectrometry, we have investigated the effects of transverse magnetic field on C_2 and CN molecules produced by laser ablation of a graphite target in nitrogen atmosphere. We found that the spectroscopic temperatures of both species, obtained *via* simulation of the optical emission spectra, as well as their emission intensities from the electronically excited states increased significantly in the presence of a magnetic field. The cyclotron radii and frequencies for electrons and ions were estimated to explain the increase in the number of collisions in the laser-produced carbon plasma plume under a magnetic field.

Key Words : Laser ablation, Magnetic field, Spectroscopic temperature

Introduction

Since the advent of lasers in 1960s, laser ablation of solid targets has been attempted to explore the interaction mechanisms between solid surfaces and high-intensity radiation.[1] Among many target materials, graphite belongs to one of the most frequently employed targets due to its fundamental importance as well as its wide applications in deposition of carbon-containing thin films such as amorphous carbon, carbon nitride, and diamond-like films.[2] For example, the historical achievement of formation of C_{60} by Smalley in mid 1980s was made possible *via* adopting laser ablation technique in vaporization of graphite in a supersonic jet source. Unlike other materials like metals and their oxides, laser ablation of graphite is unique in that clusters of various sizes are generated even under high vacuum due to the large bond energy between carbon atoms.[3]

One of the key issues in pulsed laser deposition (PLD) has been the development of techniques to manipulate the plume which consists of atoms, molecules, clusters, ions, and electrons because the properties of the films grown by PLD are in essence determined by the characteristics of the plume. In this regard, electric field was applied between a target and a substrate and it was found that the properties of the films are strongly dependent on the strength and polarity of the electric field applied.[4-6] Also, kinetic energies of ions and optical emission from neutral and ionic species in the plume changed significantly under the electric field. At first glance, it may be thought that the electric field can hardly have any influence on the plume which is electrically neutral. However, fast electrons are located at the forefront of the plume and accordingly the charge distribution in the plume is not homogeneous.[7]

As well as electric field, magnetic field can be applied to the plume with a purpose to alter its properties. Recently, a new PLD method named "Aurora PLD" was developed by Kobayashi *et al*.[8] They developed this method in order to promote the activation and/or ionization of the chemical species in the plume. It turned out that the films deposited under a magnetic field have superior quality over those deposited by conventional PLD.[8] Although there are a few results of growing thin film by PLD under a magnetic field, most of the previous works just described the changes of the properties of the deposited films, and detailed information on the plume is currently quite limited. While atoms and their ions in the plume produced in a magnetic field were investigated by several groups,[8-10] molecular species in the plume formed in the presence of a magnetic field have been rarely studied. Kokai *et al.*[11] reported the promotion of ionization of carbon atoms and enhanced formation rate of C_2 molecules by laser ablation of a graphite target in high vacuum under a magnetic field of ~0.1 T.

For a better understanding of the effect of the magnetic field on the plume, it is required to study the changes of molecular properties caused by the field in more detail. Although it was expected that the plume temperature would increase under a magnetic field due to joule heating and magnetic compression of the plume,[12] direct measurement of the temperature change induced by the magnetic field has not been reported yet. Here, we present experimental results related to the influence of a transverse magnetic field on the formation and characteristics of molecular species such as C_2 and CN in a plume generated by laser ablation of a graphite target in a nitrogen atmosphere, particularly focusing on the change of their spectroscopic temperatures by the magnetic field.

Experimental

The experimental setup is shown in Figure 1(a). A graphite target (Niraco, 99.99%) with size of 25.4 mm in diameter was used as purchased without further treatment. Two magnets (3.1 cm × 2.5 cm), apart by 1.0 cm, were mounted perpendicular to the target surface. To examine the effects of the magnetic field, the magnets were replaced with Al blocks of the same size when the plume was analyzed

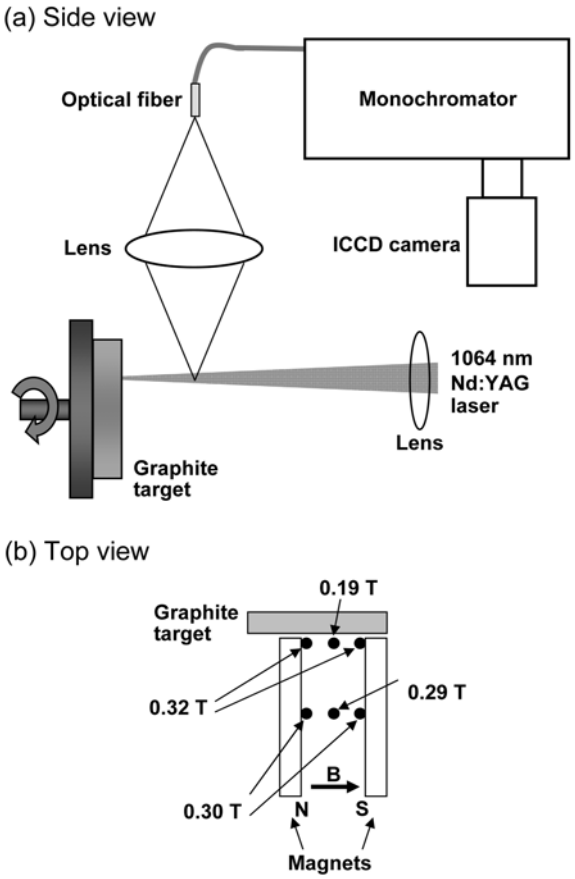

Figure 1. (a) The schematic diagram of the experimental setup. (b) The magnetic flux density, *B* in the plume expansion region.

without field. The magnetic field was measured by a pin probe and it was minimum (0.19-0.29 T) at the center and maximum (0.30-0.32 T) near the poles along the field direction as shown in Figure 1(b). As an ablation laser, a Q-switched Nd:YAG laser (λ = 1064 nm, Minilite II, Continuum, pulse duration = 6 ns) operating at 10 Hz was employed. The laser beam was loosely focused onto the graphite target placed in a vacuum chamber using a lens (focal length 30 cm) with an angle of incidence of 0°. The diameter of the focused laser spot was ~1.5 mm and the laser fluence at the target surface was estimated to be ~1.7 J/cm^2. In order to minimize a target aging effect, the graphite target was rotated by a standard rotary motion feedthrough during the experiment.

Time-resolved optical emission studies on the plume of the graphite target were done in nitrogen atmosphere. Nitrogen gas (99.999%) was fed to the chamber by a needle valve and the pressure was measured by a full range gauge (Balzers PKR250). Optical emission from the electronically excited states of C_2 and CN in the laser-produced plasma was collected using a lens of 5-cm focal length. The emission spectra were recorded at 5 mm away from the target surface, where the emission was intense enough in the pressure range chosen in our experiment and the emission intensity from the continuum transition near the target surface was negligible. The optical emission at the sampling position was fed to a monochromator coupled to an ICCD detector (Andor, DH 734) via an optical fiber bundle (Spex 700FB) as depicted in Figure 1(a). The diameter of the entrance of optical fiber bundle was 0.8 mm. The gate width of the ICCD was fixed at 50 ns.

Results and Discussion

As the graphite target is irradiated by a focused laser pulse in nitrogen atmosphere at 5 Torr, molecular emissions from the electronically excited C_2 (Swan band, $d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v=0$) and CN (Violet band, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\Delta v=0$) were dominant while those from atomic species were relatively small.[13,14] Figures 2(a) and 2(b) show optical time-of-flight spectra for C_2 and CN molecules. The optical emission signals were captured at wavelengths where the emission intensities were maximized (516.5 nm for C_2 and 388.3 nm for CN). The optical fiber probe sampled the emission signal at 5 mm away from the target. The space-resolved optical emission originates from the electronically excited molecules produced by chemical reactions or excitation of ground-state molecules *via* energetic collisions in the gas-phase plume. The excited molecules produced near the target surface may move toward the sampling position, but their

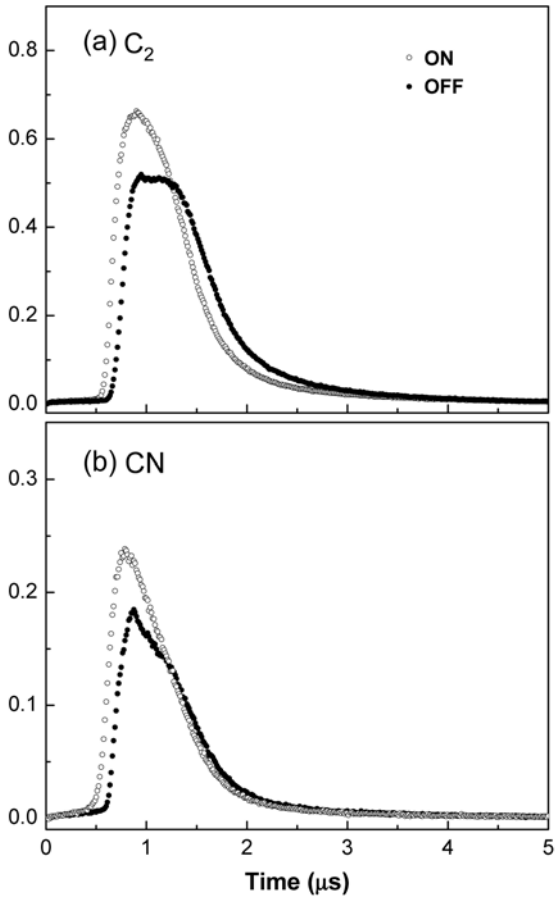

Figure 2. Optical time-of-flight spectra for (a) C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$, Δv = 0, 516.5 nm) and (b) CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, Δv = 0, 388.3 nm) with (open circle) and without (filled circle) magnetic field (B = 0.3 T) at nitrogen pressure of 5 Torr. The sampling position was 5 mm away from the target.

contribution to the optical emission intensity is negligible because the natural lifetimes of $d^3\Pi_g$ state of C_2[15] and $B^2\Sigma^+$ state of CN[16] are as short as 102 ns and 64 ns, respectively. Also, the density of molecular species near the target surface is quite low due to the high-temperature of the plasma formed upon laser ablation and they are produced mostly in the gas phase as the plasma expands. As clearly shown in Figure 2(a) and Figure 2(b), the magnetic field increased the optical emission intensity for both C_2 and CN molecules. This indicates that collisional excitation of C_2 and CN molecules and chemical reactions between atoms or molecules to produce the electronically excited molecules are enhanced by applying the magnetic field to the plume. Similar promotion of optical emission from atomic and ionic species in the plume by magnetic field was previously reported for Mg^+,[9] Al^{2+},[10] C^+, and C.[17]

In order to elucidate the effects of the magnetic filed on the temperature of the plume, we attempted to measure the change of the temperature of the electronically excited C_2 and CN molecules as they are formed in the magnetic field. It is of note that the rotational and vibrational temperatures of the excited states may differ from those of the electronically ground states, which can be measured by laser-induced fluorescence technique. The temperatures were obtained by simulation of the optical emission spectra. The details of the simulation procedure were given previously.[18] Briefly, the intensity of the optical emission spectrum, I_{cal} is given as

$$I_{cal} = C_\lambda \cdot F_{Inst} \cdot I_{v'J'v''J''}. \quad (1)$$

C_λ is a correction factor for the wavelength-dependent sensitivity, F_{Inst} is a triangular instrumental transfer function, and $I_{v'J'v''J''}$ is an optical emission signal strength for a molecular transition from $v'J'$ to $v''J''$ state. The optical emission strength, $I_{v'J'v''J''}$ is given as

$$I_{v'J'v''J''} = \frac{N_{v'J'}}{2J'+1} S_J A_{v'v''}, \quad (2)$$

where S_J is the Hönl-London factor and $A_{v'v''}$ is the Einstein coefficient. $N_{v'J'}$ corresponds to the population of excited-state molecules, which is expressed with temperatures, partitions functions, and degeneracies of the electronic, vibrational, and rotational state. The simulation of the emission spectra was performed by using the spectroscopic constants given by Pellerin *et al.*[19] and Herzberg.[20]

Typical simulations of the experimental spectra are displayed in Figure 3. The vibrational and rotational temperatures (T_{vib} and T_{rot}, respectively) of the electronically excited C_2 and CN molecules were obtained by fitting the experimental spectra. In simulation of CN spectrum as shown in Figure 3(b), the Deslandres band of C_2 near 385 nm was not included.[13] According to the simulation, T_{vib} and T_{rot} of C_2 molecules were 5100 K and 4600 K, respectively. For CN molecules, we obtained T_{rot} = 6500 K and T_{vib} = 4700 K. The large discrepancy between rotational temperatures of C_2 and CN implies the differences in their formation mechanisms; C_2 molecules are mostly formed by

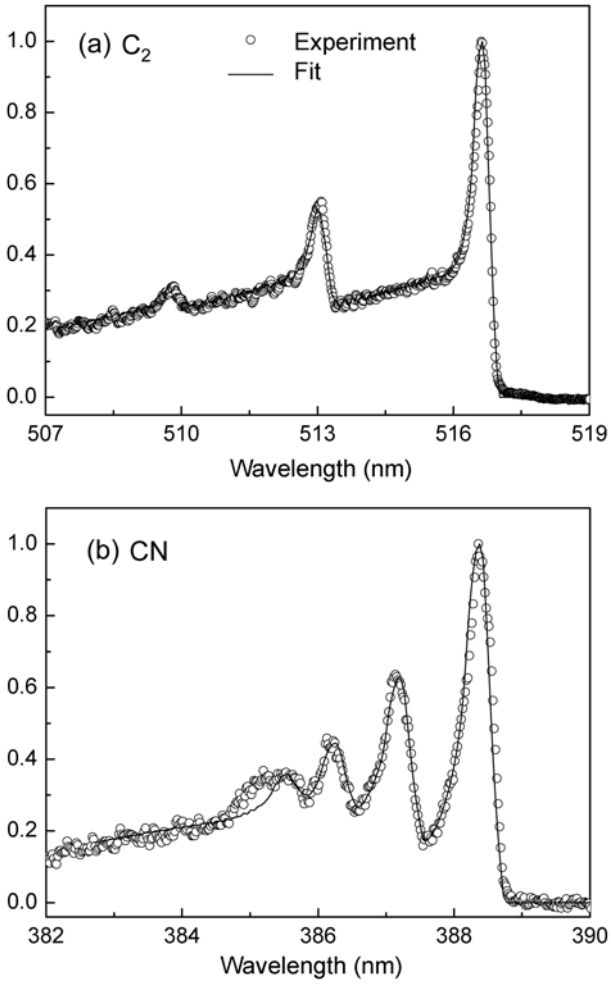

Figure 3. Typical simulation (line) and experimental spectra (open circle) for (a) C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 0$) and (b) CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\Delta v = 0$) obtained under a magnetic field (B = 0.3 T) at 1 μs after laser ablation. The sampling position was 5 mm away from the target surface. The nitrogen pressure was 5 Torr. Fitting parameters for C_2 are T_{vib} = 5100 K and T_{rot} = 4600 K and those for CN are T_{vib} = 4700 K and T_{rot} = 6500 K.

recombination of two carbon atoms, which has no activation barrier, while CN molecules are produced through energetic collisions between C_2 and N_2.[13] The $C_2 + N_2 \rightarrow 2CN$ is expected to have a nonlinear transition state, giving a large angular momentum to CN.

Spectroscopic temperatures of C_2 and CN molecules with the magnetic field on and off are shown in Figure 4. They were measured at different delay times between the ablation laser pulse and the gate pulse given to the ICCD with the sampling position of the optical fiber fixed at 5 mm away from the target surface. Intriguingly, both rotational and vibrational temperatures increased by several hundred degrees in the presence of the magnetic field. In case the laser ablation occurs under a magnetic field, the temperature of the plume is higher due to joule heating and electromagnetic compression of the plasma,[12] which also brings about the enrichment of the electronically excited species in the plasma. Electrons and ions undergo cyclotron motion in a magnetic field and, as a result, the number of collisions of

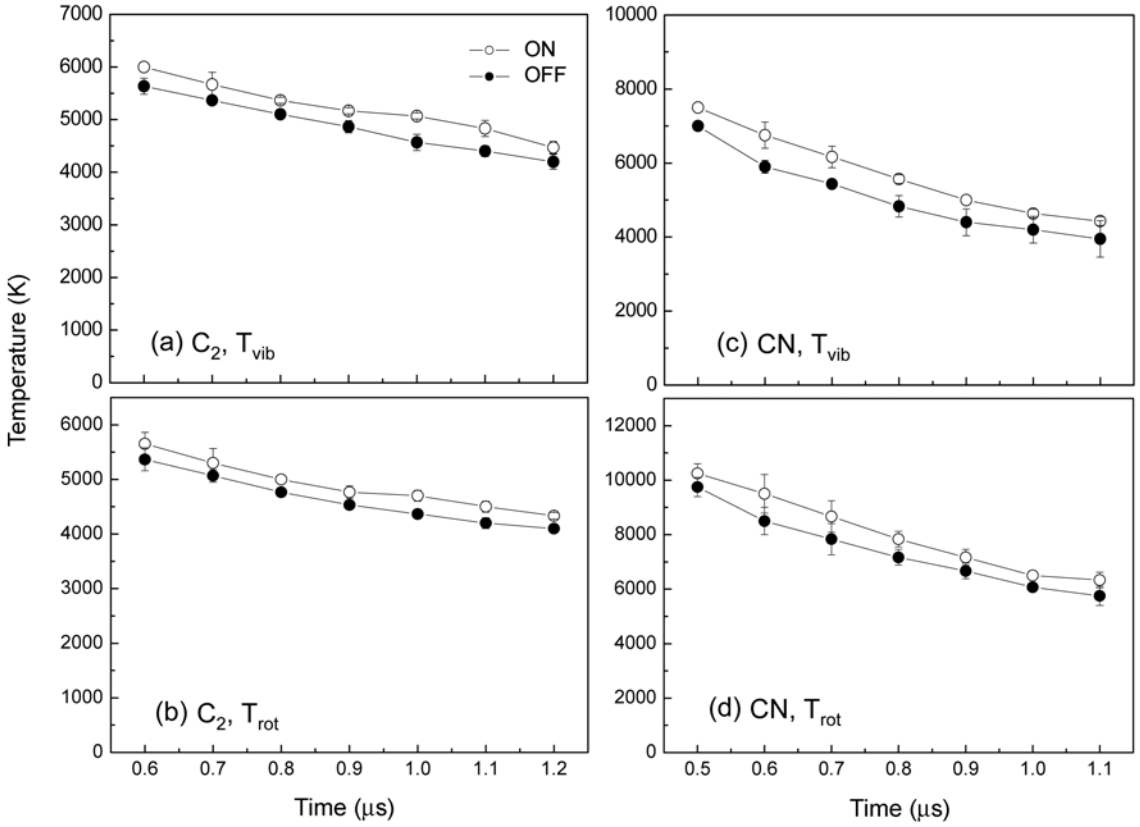

Figure 4. The change of vibrational and rotational temperatures for C_2 ((a) and (b)) and CN ((c) and (d)) molecules induced by the magnetic field. The sampling position was 5 mm away from the target surface.

charged species with atoms and molecules increases.[11] The cyclotron radius, r and frequency, f of charged species in the carbon plume can be roughly estimated from the equation $qvB = mv^2/r$, where q is the charge, v is the velocity, B is the magnetic flux density, m is the mass, and r is the cyclotron radius. The cyclotron frequency is given by $f = v/2\pi r$. In a typical carbon plasma, velocity of C^+ ions is ~10^4 m/s.[2] In general, electrons move much faster than ions in plasma. However, in a plasma produced by laser ablation of a solid target, the movements of ions and electrons are rather controlled by the transient and local electric field.[7] Therefore, we may have a *crude* assumption that the velocities of electrons and ions are roughly equal in order to compare their cyclotron radii.[11] In this case, the cyclotron radii for C^+ ions and electrons are 0.42 cm and 0.2 μm, respectively, when B = 0.3 T. The cyclotron frequencies for C^+ ions and electrons are 3.8×10^5 s^{-1} and 8.4×10^9 s^{-1}, respectively. From the above results, we can conclude that ions are not expected to respond to the magnetic field as efficiently as electrons because ions are significantly heaver than electrons. Ion-neutral reactions may contribute to the formation of molecules or clusters in the presence of a magnetic field, but the enrichment of molecular species is attributed to the increase in the density of ionic species in the plume caused by ionization of neutrals through confinement of electrons.[11] Also, it is expected that the temperature of the plume and its spatial distribution will be considerably affected by the uniformity of the magnetic field.

Conclusions

We measured the vibrational and rotational temperatures of electronically excited C_2 and CN molecules formed in a plume generated by laser ablation of a graphite target in nitrogen atmosphere with and without magnetic field. We observed, for the first time, that the spectroscopic temperatures of molecules increase when they are produced under a magnetic field. The number of electron-neutral collisions, which is responsible for the enrichment of ions and excited neutrals, increases due to the confinement of electrons and their high cyclotron frequency under a magnetic field.

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