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A SPECTROSCOPIC STUDY ON A PLUME PRODUCED BY LASER ABLATION OF GRAPHITE IN A NITROGEN ATMOSPHERE

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Abstract – A spectroscopic study on a plume produced by a reactive laser ablation of graphite in a nitrogen atmosphere was performed. As a 266 nm laser pulse irradiates the graphite target in a nitrogen atmosphere, two emission bands of C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$, Swan band) and CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, Violet band) were observed. By simulation of the optical emission spectra, spectroscopic temperatures of C_2 and CN molecules were obtained. The dependence of vibrational and rotational temperatures on the laser fluence and distance from the target as well as the pressure dependence of the emission intensities of C_2 and CN was examined to elucidate the expansion dynamics of the plume and formation mechanisms of C_2 and CN molecules

INTRODUCTION

Pulsed laser ablation (PLD) has been extensively studied in pursuit of depositing high quality thin films with the advent of lasers since early 1960s.[1] In particular, PLD has proven to be a powerful technique for deposition of multielement materials like YBCO. Recently, PLD is also applied to deposit refractory nitride films like boron nitride, gallium nitride, and carbon nitride because high temperatures well above melting points of such solid targets can be easily achieved.[1] Since the theoretical study of Liu and Cohen on the existence of superhard β- phase carbon nitride (β-C_3N_4) was reported,[2] many attempts have been made to realize this hypothetical material by using a variety of techniques including PLD. The quality of the deposited film, however, is not satisfactory yet.[3]

It is well known that the characteristics of the laser-generated plasma plume have a crucial effect on the quality and properties of the films deposited by pulsed laser ablation.[4] In this respect, information on the dynamics of laser-induced plume and the transport of the ablated species to the substrate will be of critical importance to understanding the mechanisms of pulsed laser deposition of thin films. Also, formation of clusters by condensation and production of molecular oxides or nitrides by associative chemical reactions often take place in real deposition conditions.[5] Accordingly, the growth of thin films by laser ablation is significantly affected by such gas phase chemical phenomena.

To investigate the plume expansion dynamics and gas phase reactions in the laser ablation, diverse diagnostic techniques have been employed for the last few years.[4-7] In spite of the very extensive experimental work carried out so far, many phenomena produced by laser interaction with solid surfaces, as well as the gas dynamics of the plume, are far from having satisfactory explanations and still need intensive investigations. To deposit carbon nitride films by laser ablation, a graphite target is irradiated by a focused laser beam in a nitrogen or in an ammonia atmosphere. At power densities ranging from 1 MW/cm^2 to 1 GW/cm^2, in which most practical applications of laser-material interactions fall, there is no appropriate model of laser ablation because both thermal and electronic effect have to be considered while the physics may become simpler in either lower or higher power density region.[6]

Here, we have examined the optical emission characteristics of CN and C_2 molecules formed by a reactive laser ablation of graphite in a nitrogen atmosphere to study the mechanisms relevant to the formation of molecular species. The Violet band ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) of CN and Swan band ($d^3\Pi_g \rightarrow a^3\Pi_u$) of C_2 were recorded at different laser fluences. The vibrational and rotational temperatures of the molecules were determined by simulation of the emission spectra. The expansion dynamics of the plume was also studied by analyzing the spectra at different positions, laser fluences, and pressures.

MATERIALS AND METHODS

The experimental setup is depicted in Fig. 1. In the laser ablation experiment, graphite targets (Niraco, 99.99%) with size of 20 mm in dia. were used as purchased without further treatment. The fourth harmonic of an Nd:YAG laser (266 nm, Quanta-Ray GCR 150-10) was used to impinge the target. The target was rotated by a standard rotary motion feedthrough. The targets were frequently replaced to ensure signal reproducibility, avoiding the aging effect caused by repetitive irradiation of high intensity pulsed laser. The laser beam was focused onto the graphite target by a S1UV lens with focal length of 30 cm. Optical emis-

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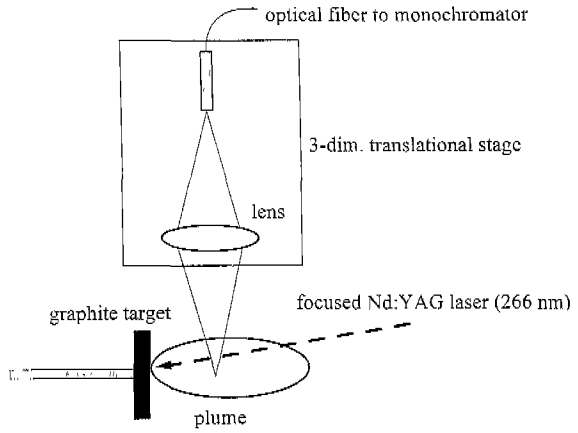

Figure 1. The schematic diagram of the experiment.

sion studies on the laser-generated plume of graphite target have been done in a 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).

The optical emission from laser-generated plume was imaged onto the optical fiber (Spex 700FB) by a lens of 15 cm focal length (f=3.7) and sent to a monochromator (Jobin-Yvon, TMR1000) coupled to a photomultiplier tube (R928). Spatially resolved measurements of the emission spectra were performed by translating the receiving end of the optical fiber within the image of plasma. The signal from the photomultiplier tube was fed to an oscilloscope (LeCroy 9300) and a boxcar averager (SR250) was used for the signal processing. The monochromator was calibrated by using a Hg lamp (Oriel 6335). The correction of the emission spectra for the spectrometer spectral response was not attempted since the scan range of each emission spectrum was as narrow as 4 nm.

Simulation of the emission spectra has been attempted by adopting a standard procedure[8] to deduce the rotational and vibrational temperatures of C_2 and CN. The spectroscopic constants given by Pellerin *et al.*[9] and Herzberg[10] were used for C_2 and CN, respectively. The intensity of the simulated spectrum, I_{cal} is given as

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

C_λ is a dimensionless correction factor for the wavelength-dependent sensitivity of the detection system. Since the simulation range was narrow enough in our experiment, the wavelength-dependence of C_λ was neglected and C_λ was used just as a multiplicative scaling factor. F_{Inst} is a triangular instrumental transfer function which is determined by the slit width of the monochromator. $I_{\nu'J'\nu''J''}$ is an optical emission signal strength for radiation produced by a molecular transition from $\nu'J'$ to $\nu''J''$ state, which can be written as

$$I_{\nu'J'\nu''J''} = \frac{N_{\nu'J'}}{2J'+1} S_J E^3_{\nu'\nu''} R^2_{e\,q_{\nu'\nu''}}, \quad (2)$$

where $N_{\nu'J'}$ is the number of molecules in excited-state and S_J is the Hönl-London factor. $E_{\nu'\nu''}$ is the difference of energy between the vibrational states $\nu'$and ν''. R_e is the electron transition moment which is considered as a constant, and $q_{\nu'\nu''}$ is

$$N_{\nu'J'} = \left(\frac{No}{Q_E Q_{\nu'} Q_{J'}}\right) g_E \cdot e^{-\frac{E_I}{kT_I}} \cdot g_{\nu'} e^{-\frac{E_{\nu'}}{kT_{\nu'}}} \cdot g_{J'} e^{-\frac{E_{J'}}{kT_{J'}}}, \quad (3)$$

Franck-Condon factor.

At thermal equilibrium, the number of molecules in the excited state is defined as

where E_i (i=E, v', J') is the electronic, vibrational or rotational energy of the upper state. T_i, Q_i, and g_i are the corresponding temperature, partition function, and degeneracy. k is the Boltzmann constant and N_0 is total number density.

RESULTS AND DISCUSSION

In the spectral range of 370-525 nm, emission bands from C_2 and CN molecules were observed. Emissions from N, N^-, C, C^+, and N_2^+ were not observed in our experimental conditions,[11] presumably hidden in the vibrational progressions of C_2 and CN, if any. Fig. 2 and Fig. 3 show typical emission spectra of C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 0$) and CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\Delta v = 0$), respectively. The filled circles represent experimental data and the lines are the simulated spectra. Two vibrational sequences with band heads at 388.3 nm ($\Delta v = 0$) and 421.6 nm ($\Delta v = -1$) belong to the Violet system ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) of CN. Three vibrational sequences with band heads at 516.6 nm ($\Delta v = 0$), 473.7 nm ($\Delta v = 1$), and 438.2

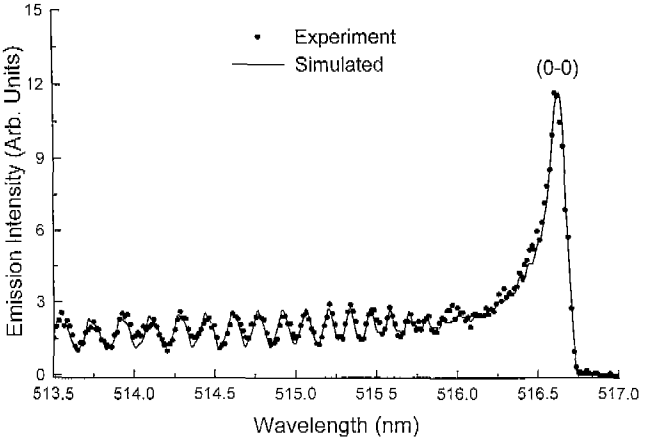

Figure 2. Emission spectra of C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$, Swan band (0,0)) produced by laser ablation of graphite in N_2 at 266 nm. The lines are the simulated spectra and the filled circles are the experimental data. The laser fluence was 4.5 J/cm^2. The pressure of N_2 was 10 Torr and the distance from the target was 1.5 mm.

nm ($\Delta v = 2$) correspond to the Swan bands of C_2. The vibrational sequences with $\Delta v = 0$ for the Violet and Swan bands were selected to simulate the emission spectra.

The vibrational and rotational temperatures of CN molecules in the excited state were inferred by fitting the experimental spectra. For C_2, only rotational temperature was obtained since the emission intensities for the transitions except

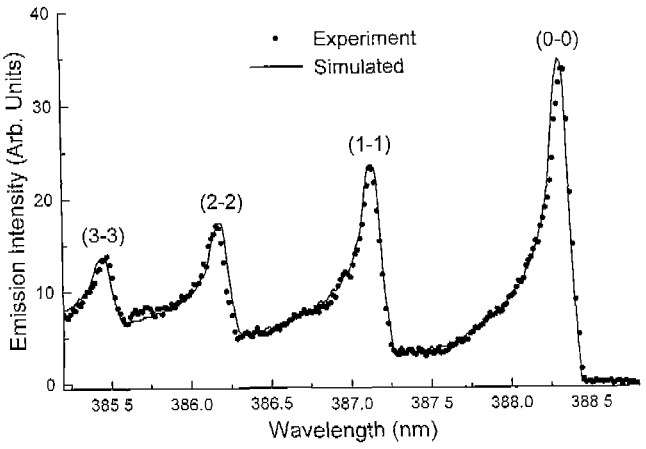

Figure 3. Emission spectra of CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, Violet band (0,0)) produced by laser ablation of graphite in N_2 at 266 nm. The lines are the simulated spectra and the filled circles are the experimental data. The laser fluence was 4.5 J/cm^2. The pressure of N_2 was 10 Torr and the distance from the target was 1.5 mm.

(0,0) transition of $\Delta v = 0$ were not large enough. Because the excitation thresholds are 2.4 eV and 3.1 eV for the C_2 Swan band and the CN Violet band, respectively, the emission intensities may also be considered to describe the behaviors of the ground state concentrations of each species.[12]

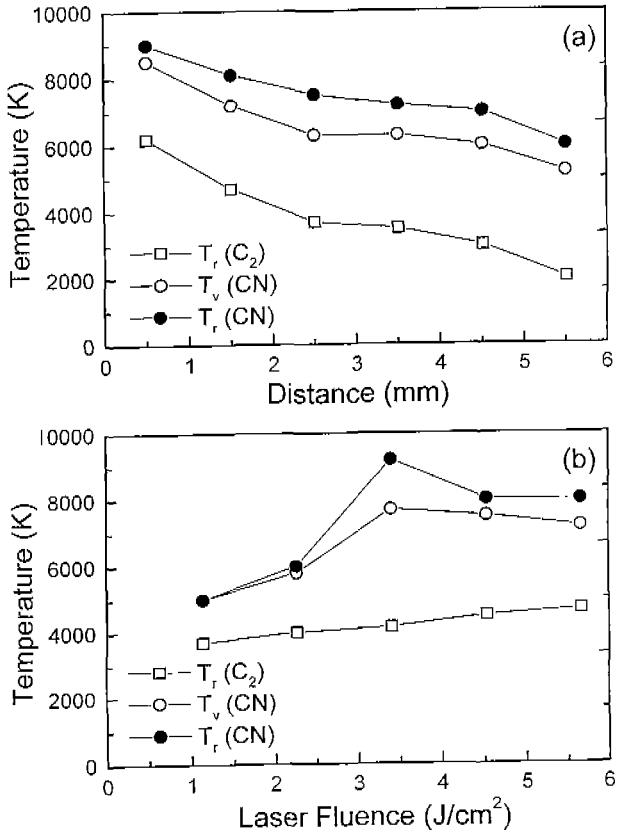

Figure 4. Temperatures of C_2 and CN molecules *vs.* (a) the distance from the target and (b) the laser fluence. T_r and T_v are the rotational and vibrational temperature, respectively. The laser fluence was 4.5 J/cm^2. The pressure of N_2 was 10 Torr.

Fig. 4(a) shows the spatial evolution of temperatures, which was obtained by recording the emission spectra at different distances, d (d = 0.5-5.5 mm) from the target. Monotonous decrease of vibrational and rotational temperatures with increasing distance was observed. The temperatures decrease because C_2 and CN molecules undergo collisions with the surrounding gas as the plume expands. In particular, the cooling of the plasma is manifested by the drastic decrease of C_2 rotational temperature.[13] The rotational temperature of CN molecules is lower than the vibrational temperature as observed by Dinescu et al.[13] But oscillation of temperatures with the position previously reported[13] was not found. The dependence of temperature on the laser fluence is shown in Fig. 4(b). At lower laser fluences, vibrational and rotational temperatures of CN molecules increase with increasing laser fluence. The saturation or decrease of CN temperature at higher laser fluence indicates that collisional dissociation or ionization is dominant, causing a net decrease of population in the higher vibrational levels.[14]

C_2 molecules are considered to be formed by the recombination of two C atoms with M as a collision partner, which has no activation barrier.[6] Fig. 5 shows the pressure

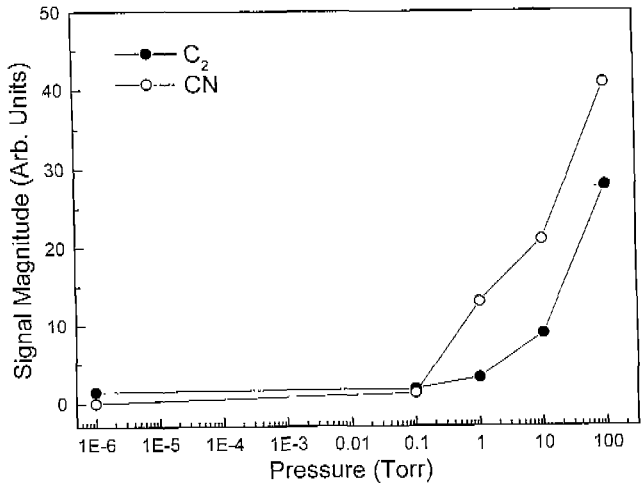

Figure 5. The emission signal magnitude *vs.* nitrogen pressure. The signal magnitude was obtained by integration of the total emission intensity of $d^3\Pi_g \rightarrow a^3\Pi_u$ Swan band and $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ Violet band of C_2 and CN, respectively. The laser fluence was 4.5 J/cm^2 and the distance from the target was 1.5 mm.

dependence of the integrated emission intensity of C_2 and CN. A drastic enhancement of the emission intensity with the ambient pressure reflects that C_2 molecules are mainly produced by the recombination. The rotational temperature of CN is higher than that of C_2, which indicates that CN molecules are produced by energetic collisions.[15] CN molecules are thus expected to be formed by the following reactions:

$$C + C + M \rightarrow C_2 + M \quad (4)$$

$$C_2 + N_2 \leftrightarrow 2CN \quad (5)$$

Since the bond energies of reactants and products of the reac-

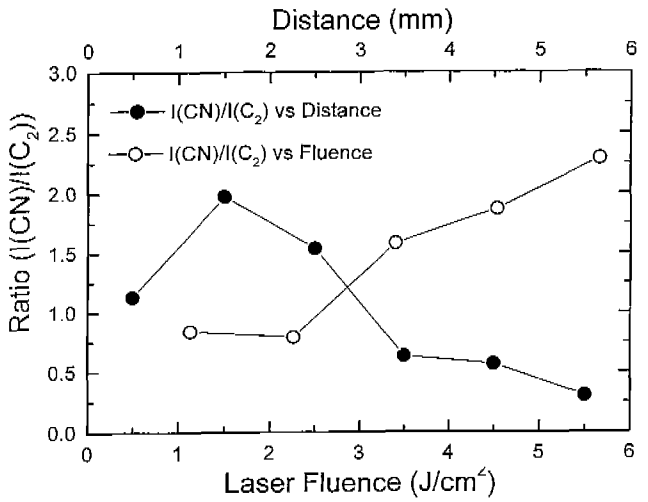

Figure 6. The ratio of emission intensity, $I(CN)/I(C_2)$ *vs.* the distance from the target and the laser fluence. T_r and T_v are the rotational and vibrational temperature, respectively. The laser fluence was 4.5 J/cm^2. The pressure of N_2 was 10 Torr.

tion (5) are approximately equal, the forward and backward reaction rates of the reaction (5) are essentially determined by the collision frequencies.[15] Therefore, CN molecules are produced at early times of plume propagation when C_2 density is high. Considering the high rotational temperature of CN, the possibility of CN formation on the graphite surface is neglected.

Fig. 6 illustrates the relative enrichment of CN over C_2 with increasing distance or laser fluence. The ratio of emission intensity, $I(CN)/I(C_2)$ decreases with distance in general because C_2 molecules are mostly formed by recombination of C atoms. The density of C_2 decreases with distance because the density of C atoms decreases as the plume expands. Near the target (d = 5 mm), density of CN is low because CN is formed by collisions of C_2 and N_2. C_2 density decreases with distance faster than CN because the bond energy of C_2 (6.25 eV) is smaller than that of CN (7.75 eV), allowing CN molecules to survive the high temperature of the plume. The ratio of emission intensity $I(CN)/I(C_2)$ increases with laser fluence due to photodissociation of C2 and reduction of recombination rate at higher plume temperatures.[13]

CONCLUSION

By fitting the optical emission spectra, spectroscopic temperatures of diatomic molecules like C_2 and CN produced by laser ablation of graphite in a nitrogen atmosphere were estimated. Because CN molecules were formed by energetic collisions between C_2 and N_2 molecules in the gas phase, the temperature of CN was higher than that of C_2. A significant cooling of the plume as it expands was manifested by a spatial evolution of temperatures. Also, relative enrichment of molecular species was found to be significantly dependent on the laser fluence and the distance from the target.

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