Time-resolved optical emission studies on the laser ablation of a graphite target: The effects of ambient gases

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Time-resolved optical emission spectroscopy was employed to examine the temporal properties of a plume formed by laser ablation of a graphite target in He, N₂, and Ar background gases. Time-dependent spectroscopic temperatures of electronically excited C₂ and CN molecules generated in the plume at different background gases and pressures were derived by simulation of the emission spectra. The rotational temperature of CN molecules was significantly higher than the vibrational temperature. This indicates that they are formed in the gas phase by the chemical reaction C₂ + N₂ → CN. At pressure above 0.5 Torr, the temperature in each background gas was apparently in the order of Ar > N₂ > He while there was no such gas dependence at 0.1 Torr. The expansion dynamics and cooling rate of the plume turned out to be highly dependent on the background gas and its pressure. © 2005 American Institute of Physics. [DOI: 10.1063/1.1925336]

I. INTRODUCTION

Pulsed laser deposition (PLD) has been extensively studied to deposit a variety of functional materials such as high-temperature superconductors, diamondlike carbon, carbon nitride, silicon carbide, and Er-doped silicon. In PLD, there are several experimental parameters such as laser wavelength and its fluence, target-to-substrate distance, temperature of a substrate, and background gas and its pressure, all of which have significant influence on the characteristics of the deposited films. Among these parameters, the choice of the background gas is often confusing, in particular, when certain reactive gas such as nitrogen or oxygen is not required as in the deposition of nitride and oxide films, respectively.

A common choice of a background gas, in many nonreactive PLD, is He or Ar. Although both He and Ar are categorized into inert gases, the formation and expansion mechanisms of a laser-induced plasma, so-called “plume,” in He and Ar background gases are quite dissimilar due to the differences in momentum-transfer and hydrodynamical effects as reported by Wood et al. In addition, the size of the grains, surface morphology, and thickness of the grown films show significant dependence on the background gas and its pressure. On the other hand, desired film qualities, in some cases, may be achieved by PLD in high vacuum.

Over many trial and errors, anyhow, one would ultimately find an optimum gas and pressure to meet his or her unique purpose. However, it would be certainly meaningful to try to understand the effects of different background gases in PLD since not only dynamical but also qualitative properties of the plume, such as temporal or local temperatures and chemical reactions there in, are highly affected by the choice of the ambient gases and their pressures.

In this work, we present experimental results that display a strong dependence of expansion dynamics and spectroscopic temperatures of a plume generated by laser ablation of a graphite target on background gases and their pressures. Laser ablation of graphite has been extensively studied aiming at either deposition of functional materials such as diamondlike carbon, carbon nitride, and carbon nanotube or producing carbon clusters including C₆₀. Also, the graphite target belongs to one of the most suitable targets to examine basic plasma dynamics since not only atomic but also molecular species are abundant in the carbon plasma due to the high binding energies of C₂ or CN. We employed an optical emission spectroscopy to obtain space- and time-resolved spectra from electronically excited C₂ and CN molecules produced by laser ablation of a graphite target in He, N₂, and Ar. Rotational and vibrational temperatures of the molecules were derived via simulation of the spectra. Although the formation of C₂ or CN molecules by laser ablation of graphite and their optical emission spectra were widely investigated, the dependence of their temperatures on different background gases and pressures has been rarely reported.

II. EXPERIMENT

The experimental setup was described previously. In this experiment, an intensified charge-coupled device (CCD) array detector was adopted, replacing a photomultiplier, with a goal to obtain time-resolved spectra. A Q-switched Nd:YAG (yttrium aluminum garnet) laser (Quanta-Ray, λ = 1064 nm, pulse duration=8 ns) operating at 10 Hz was loosely focused onto a graphite target (Nilaco, 99.99%) placed in a vacuum chamber using a lens (focal length 50 cm) with an angle of incidence of 45°. The diameter of the focused laser spot was ~1.6 mm and the laser fluence at the target surface is estimated to be 2.8 J/cm². The graphite target was rotated by a standard rotary motion feedthrough to reduce a target aging effect. The chamber was filled with He, Ar, or N₂ and the gas pressure was varied from 0.1 to 10 Torr.
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or CN molecules were observable in the gas phase even 1
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III. RESULTS AND DISCUSSION

Optical emission from electronically excited states of C

and CN molecules in a plume generated by laser ablation

was collected using a lens of 5-cm focal length. The emis-

sion spectra were recorded at 5 mm away from the target

surface, where the emission was intense enough in the pres-

sure range chosen in our experiment and the continuum

emission near the target surface was not collected. The opti-

cromat coupled to an ICCD detector

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sures chosen in our experiment and the continuum

spon spectra were recorded at 5 mm away from the target

surface, where the emission was intense enough in the pres-

ure range chosen in our experiment and the continuum

mission near the target surface was not collected. The opti-

cromat coupled to an ICCD detector (Andor, DH 734) via

on an optical fiber bundle (Spex 700FB). The diameter of

the entrance of the optical fiber bundle was 0.8 mm. The gate

width of the ICCD was fixed at 50 ns.

FIG. 1. Time-resolved optical emission spectra of C

(Swan band, d 3Πu
→a 3Πv, Δν=0) and CN (Violet band, B 2Σ+→X 2Σ+, Δν=0) molecules at

(a) Ar 5 Torr and (b) N2 5 Torr, respectively. The emission was sampled at 5

mm away from the target surface. The laser fluence was 2.8 J/cm².

FIG. 2. Normalized peak emission intensity of (a) C2 at 516.5 nm and (b)

CN at 388.3 nm vs delay time at 5 Torr.

dependent concentrations of the molecular species but also

their excitation efficiencies at the sampling position since the

optical emission intensities are determined by the concen-

tration of the electronically excited species.

Normalized optical emission intensities from the elec-

tronically excited C2 and CN in different background gases

are shown in Fig. 2. For molecular species such as C2 and

CN, it is not possible to obtain their velocities by adopting

optical time-of-flight method that were often applied to get

velocities of atomic species generated by laser ablation.

Since molecules are produced mostly in the gas phase, not in

front of the target surface where the temperature is very

high, the spectra shown in Fig. 2 are not optical time-of-

flight spectra, to be precise. Still, we can get information on

the gas-dependent transport phenomena of the ejected atoms

and postproduced molecular species including their elec-

tronic excitation processes. For instance, it is expected to get

information on a position of a contact front, a surface that

separates the ablation plume from the background gas, which

is in essence determined by the speed of sound of the back-

ground gas.

In Fig. 2(a), peak emissions from C2 in He, N2, and Ar

are observed at 0.6, 0.9, and 1.0 μs, respectively, which

manifests that the plume formed in He expands farther than

N2 and Ar at a given delay time because all the emissions

were measured at the same position. This conforms to the

fact that the velocities of sound for the three background

gases chosen in our experiment are in the order of He > N2

>Ar. Although the formation mechanisms for C2 and CN

that were produced by laser ablation of a graphite target in

N2 atmosphere are different to each other, 13 the peak arrival

times that give the maximum emission intensity for C2 and

CN are in essence determined by the gas dynamic effect and
thus are nearly the same as shown in Figs. 2(a) and 2(b). The pressure dependences of the peak arrival times for He, N\textsubscript{2}, and Ar background gases are shown in Fig. 3. At 0.1 Torr that is certainly below the acoustic regime, the peak arrival times are estimated to be \(\sim 500\) ns for the three different gases. With an increase in the background gas pressure, the times are no longer equal to each other. It takes the longest time for the plume to expand and the pressure effect is most distinct in the heaviest Ar gas among the three.

Figure 4 shows the experimental and simulated spectra of \(\text{C}_2\) \((d^{3}\Pi_g \rightarrow a^{3}\Pi_u, \Delta \nu=0)\) and \(\text{CN}\) \((B^{2}\Sigma^+ \rightarrow X^{2}\Sigma^+, \Delta \nu=0)\) bands. The vibrational and rotational temperatures of the electronically excited \(\text{C}_2\) and \(\text{CN}\) molecules were obtained by simulation of the experimental spectra.\textsuperscript{12} The spectroscopic constants used for simulation of the emission spectra were obtained from the previous works.\textsuperscript{20,21} The maximum error in the derivation of the spectroscopic temperatures via simulation of the spectra is estimated to be approximately 500 K. The error was even larger at early times of plume expansion due to the low emission intensity and the interference from the scattered continuum emission. At times shorter than 200 ns, the simulations did not fit the experimental spectra thereby. This may stem from the non-Boltzmann vibrionic distributions in the electronically excited states as well as the above-mentioned problems.

The vibrational and rotational temperatures of the electronically excited \(\text{C}_2\) molecules produced in He, N\textsubscript{2}, and Ar background gases at various pressures showed a decreasing character as illustrated in Figs. 5 and 6, respectively. The vibrational temperature of \(\text{C}_2\) molecules in the plume front, emitting fluorescence at the sampling position (5 mm away from the target) at 200 ns, was as high as 15 000 K. The temperature of \(\text{C}_2\) molecules that reached the sampling position thereafter decreased rapidly until \(\sim 800\) ns. The decreas-
ing trends of both temperatures with the delay time were nearly identical for Ar and N$_2$ gas at pressures above 0.5 Torr. However, the trends at 0.1 Torr were rather close to that for He gas. This can be understood as follows. The contact front between the plume and background gas is not so sharp when the pressure or the mass of the background gas molecules is low and the plume just cools down as it expands. In the other case, the temperature at a given position decreases less rapidly since the confined plume expands more slowly. Also, a fair amount of kinetic energy is converted to heat due to mutual penetration of laser plasma and ambient gas with increase in the ambient gas pressure.$^{22}$

The vibrational and rotational temperatures of CN molecules at various pressures of N$_2$ are shown in Fig. 7. The vibrational temperatures of CN molecules at times shorter than $\sim$1 $\mu$s were lower than those of C$_2$ molecules while they become nearly identical at 2 $\mu$s. Since C$_2$ molecules, formed by recombination of carbon atoms, act as precursors of CN molecules via a chemical reaction C$_2$+N$_2$→CN,$^{13}$ formation of CN is delayed in time. Since CN molecules are formed in a less hot region of the plume, the temperature of CN is lower than that of C$_2$. Such difference in the formation mechanisms may explain why there is no distinct difference in the decreasing trend of the vibrational temperature at 0.1 Torr and that at pressures above 0.1 Torr as observed in C$_2$ formed in Ar and N$_2$. On the other hand, the rotational temperature of CN was substantially higher than that of C$_2$ because of the chemical reaction, C$_2$+N$_2$→CN, which is expected to have a nonlinear transition state to result in a large angular momentum of the product, CN. As a result, the vibrational temperature of CN was higher than the rotational temperature by several thousand degrees over the pressure range from 0.1 to 10 Torr as shown in Fig. 8.

Figure 9 shows the dependence of spectroscopic temperatures of the electronically excited C$_2$ molecules on the ambient gas pressure. At 0.1 Torr, both rotational and vibrational temperatures were nearly independent on the gas type. At pressures above 0.5 Torr, the temperatures were appar-

![FIG. 6. Rotational temperatures of C$_2$ molecules at different background gas pressures for He, Ar, and N$_2$.](image)

![FIG. 7. Vibrational and rotational temperatures of CN molecules at different pressures of N$_2$.](image)

![FIG. 8. The variation of rotational and vibrational temperature of CN molecules at 500-ns delay time as a function of the pressure.](image)
The temperature remained almost unchanged. This indicates that the rotational energy of the hot C₂ molecules is more efficiently transferred to the ambient gas via gas kinetic collisions than the vibrational energy.²³

IV. CONCLUSIONS

The background gas effects on temperatures and expansion dynamics of a plume generated by laser ablation of a graphite target were investigated by employing a time-resolved optical emission spectroscopy. The expansion of the plume was monitored by measuring the temporal emission intensities of C₂ and CN molecules in the plume and their rotational and vibrational temperatures were estimated by simulation of the spectra. The expansion of the plume was largely dependent on the mass of the background gas: the plume expands farther at lower mass and pressure. There was no gas dependence on spectroscopic temperature at 0.1 Torr. At pressures above 0.5 Torr, however, the temperature in each background gas was in the order of Ar > N₂ > He. The rotational temperature of CN molecules was significantly higher than their vibrational temperature. This confirms that CN molecules are formed in the gas phase by the chemical reaction C₂ + N₂ → CN, through which CN obtain large rotational angular momentum.

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