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Optical spectroscopy of emission from CN plasma formed by laser ablation

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Abstract
The characterization of a plasma plume is a key issue in laser ablation and deposition studies. The formation, composition and propagation of laser-produced plasmas used for pulsed laser deposition (PLD) of CN have been studied under film growth conditions. The plume was generated by focusing 1064 nm, 9 ns pulses from Nd:YAG laser on carbon target under nitrogen ambient. We investigated the different species, such as CII, CI, C_2, NII and CN, in laser ablated CN plasma using optical emission spectroscopy. The spectral characteristics of the plasmas were measured to determine the plasma properties as gas pressure was changed from 10^{-5} to 90 mTorr. The intensities of molecular species did not depend on gas ambient whereas ion intensities did. The vibrational temperature shows dependence with gas pressure.

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1. Introduction

Pulsed laser deposition (PLD) has been broadly used to grow a variety of carbon-containing refractory films, such as diamond-like carbon (DLC) [1], carbon nitride [2, 3] and, silicon carbide [4]. In particular, since the theoretical study by Liu and Cohen [5], 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 film growth are mostly affected by laser-ablation plasma, the so-called 'plume' produced by irradiation of a target using a high-energy 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 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.

It is believed that the dynamics of the ablation plume and the behavior of the plume species strongly affect the deposition process and consequently, the properties of the deposited films. When the deposition is performed in a reactive ambient, in addition, the chemical reactions of the ablated species with the species in the reactive ambient play a crucial role in film deposition. Hence, the characteristics of the plume produced by pulsed laser ablation and the understanding of the processes involved in film deposition are of great interest. There are several techniques for characterizing the ablation plume. Among them optical emission spectroscopy (OES) is an effective one for *in situ* examination of the processes occurring in the gaseous phase and characterization of the plume accompanying pulsed laser ablation and film deposition [6].

The PLD of graphite carbon target in high vacuum condition and nitrogen ambient gas using Nd:YAG laser allows one to produce carbon films with smooth surface and high degree of diamond structure. Furthermore, the physical and optical properties of DLC and carbon nitride films can be varied changing the deposition conditions. In this work, we studied the plume produced from graphite ablation in vacuum and nitrogen plasma with the OES technique.

2. Experimental setup

The experimental setup and experimental procedure were described previously [2, 7]. We used a short-pulse, Q-switched Nd:YAG laser which provided 7 ns, 500 mJ laser pulses at a wavelength of 1064 nm with a 10 Hz repetition rate. The experiment took place in a stainless steel vacuum chamber configured as a six-way cross of 10 cm inner diameter tubes forming a central 10 cm diameter target chamber evacuated to 10^{-5} mTorr, and flushed with pure

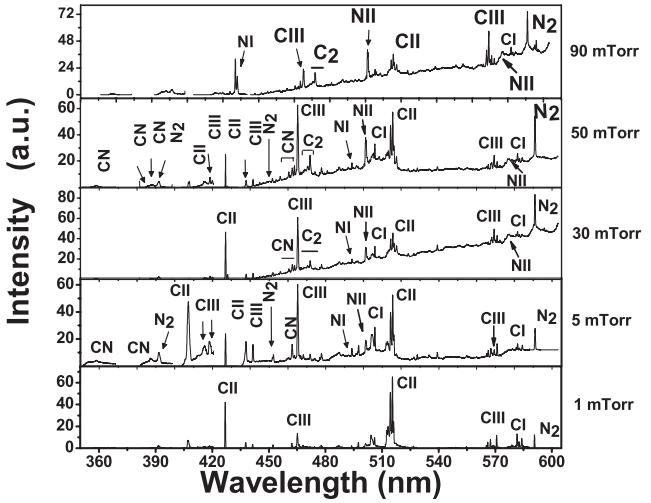

Figure 1. Emission spectra of the graphite plume in nitrogen ambient, at a fluence of 10 J cm^{-2} for different pressures.

nitrogen (99.999) at different flow rates during experiments. The laser beam was focused with a 20 cm focal length lens on a graphite target (99.99%) with a 45° angle of incidence, giving an energy density of approximately 10 J cm^{-2}. Nitrogen gas (99.999%) was injected into the chamber as a reactive gas, and the flow of it was accurately controlled by a needle valve. During laser ablation, nitrogen pressure was varied from 1 to 90 mTorr as measured by a vacuum gauge. The substrate was placed at a distance of 30 mm from the target. The films were deposited on silicon substrates that had previously been ultrasonically cleaned in acetone. Emission spectra were collected, imaged onto spectrograph TRIAX 550 with 1200 grooves mm^{-1} grating and a resolution of 0.025 nm using two 10 and 13 cm focal length lenses positioned outside the reactor. For time-integrated spectra measurements, the spectrograph was equipped with a CCD linear sensor (1024 × 256). Most of the spectra were collected with integration times of 1 s.

3. Results and discussion

Radiation emitted by laser-produced plasma during ablation of graphite target in vacuum and nitrogen ambient at different pressures is collected in 350–600 nm range. In all cases, a very luminous plasma is obtained and expands between the target and the substrate. All our spectra were taken in the proximity of the target. These spectra were characterized by a strong continuum emission, originating from free–free or free–bound transition and favors at early stage of expansion the reabsorption of plasma species and overlaps the excited species in the neighborhood of the target.

Figure 1 displays the emission spectra of the plume created from graphite target ablation in nitrogen plasma, taken at a distance of approximately 1 cm from the target, over a range from 350 to 600 nm at a fluence of 10 J cm^{-2} at a wavelength of 1064 nm and 7 ns energy pulse for different nitrogen pressures.

The identified emission lines originate almost from mono-atomic species (CI and NI) and ionized species (CII, CIII and NII). In addition, emission bands from diatomic C_2 Swan system (transition $d\,^3\Pi_g \rightarrow a\,^3\Pi_u$, $\Delta\nu = 0 : 516.5$ nm; $\Delta\nu = +1 : 473.7$ nm) and CN violet system (transition $B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+$, $\Delta\nu = -1 : 421.6$ nm; $\Delta\nu = 0 : 388.3$ nm; $\Delta\nu = +1 : 359.0$ nm) are clearly apparent. The vibrant $\Delta\nu = 2$ emission of the CN violet system and $\Delta\nu = 1$ of C_2 Swan system slightly increase in this pressure range. However, the emission intensity of the spectra from these molecular species was very weak when compared with other monoatomic species. As reported, the expansion of the plume is limited at high pressures and the plume is spatially confined [8, 9]. Consequently, dissociation rates of CN molecules overtake formation rates at high pressures given the increased number of energetic collisions in the plume.

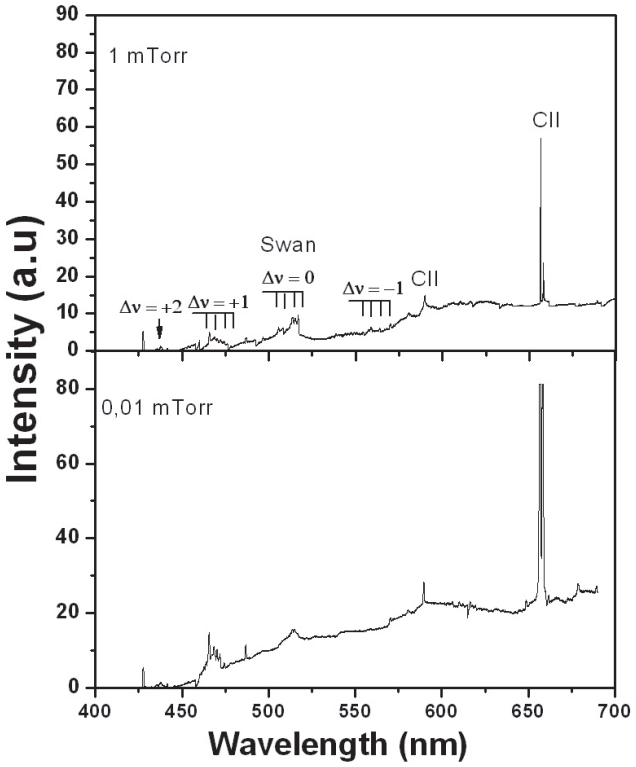

Figure 2. Emission spectra of the graphite plume in vacuum, at a fluence of 10 J cm^{-2} from different pressures.

Figure 2 shows spectra emissions of carbon plasma in vacuum at different pressures. These spectra are dominated by C_2 Swan system ($d\,^3\Pi_g \rightarrow a\,^3\Pi_u$) of the sequence ($\Delta\nu = +2, +1, 0$) followed by CII and CI. Neutral carbon lines CI are not prominent in our spectra. In both spectra, singly ionized CII lines were found at 513.4, 515.1 and 589.16 nm, whereas doubly ionized CIII line at 465.58 nm. No obvious features belonging to the Delandres–D'Azambuja singlet system for C_2 ($C\,^1\Pi_g \rightarrow A\,^1\Pi_u$) were visible between 350 and 420 nm. We did not observe significant differences in emission spectra of the plumes expanding in vacuum or at 1×10^{-2} mTorr. It is clearly seen that these two spectra are almost the same.

3.1. Estimation of vibrational temperature

The estimation of vibrational temperature of the carbon plasma was done according to the Boltzmann distribution:

$$\ln \sum_{\nu''} (\lambda^4 I_{\nu'\nu''}) = C - G(\nu') \frac{hc}{\kappa T_{\text{vib}}}, \qquad (1)$$

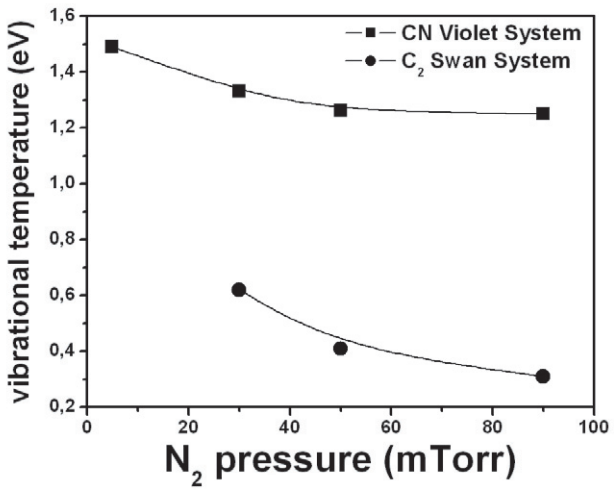

Figure 3. Dependence of the vibrational temperature of CN and C_2 molecules on the nitrogen ambient at different pressures and 10 J cm^{-2}.

where λ is the wavelength corresponding to the emission, h Planck's constant, c the velocity of light, C a constant, $G(v')$ the term value corresponding to the vibrational level in the upper electronic state and T_{vib} the vibrational temperature. Under the assumption that the carbon plasma are in local thermodynamic equilibrium, the vibrational temperature for bands C_2 Swan ($\Delta v = 1$, in the 467–474 nm range) and CN violet ($\Delta v = 2$, in the 450–460 nm range) systems, respectively, were calculated from the sums of the band-head strengths measured in various v' or v'' progressions against the vibrational term values $G(v')$ [10]. The spectroscopy constants $G(v')$ used for calculations were obtained from the handbook [11].

The dependence of the vibrational temperature of CN and C_2 molecules on the nitrogen ambient at different pressure are given in figure 3. From this figure, we notice that the increase in nitrogen pressure decreased the vibrational temperature of the CN and C_2 species. This could be explained by the fact that the nitrogen atmosphere cooled the hot electrons as well as excited states of molecules by collisions leading to a more efficient thermalization. We also note that CN molecules are vibrationally much hotter than C_2. This is attributed to the fact that CN molecules are formed by energetic collisions of C_2 and N_2, whereas C_2 molecules are mostly generated by recombination of carbon atoms with a non-activation barrier in the gas phase [12].

4. Conclusion

C_2 emission bands can be usually observed from the plume generated from graphite ablation in nitrogen ambient. In our case, however, the optical emission of the plume in vacuum changes with pressure. In vacuum it is dominated by emission lines from monoatomic carbon atoms and ions and turns gradually for higher pressures to be dominated by emissions from C_2 molecules, whereas those from carbon atoms and ions disappear at higher pressure. The relative concentration of atomic species depends on the gas pressure.

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