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Optical Emission Study of Laser Ablation Plasma Plume for the Preparation of Diamond Films in Oxygen Atmosphere

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Spatially and time-resolved optical emission analysis was carried out on the plasma plume produced by KrF excimer laser ablation of graphite in various oxygen atmospheres. The visible plasma plume was dominated by emission of C_2 molecule and C atom. Emission of C_2 Swan system was strongly observed near the substrate under the diamond growth conditions previously reported [Nature, **399** (1999) p.340]. From the time-resolved emission study, ablated particles were found to have the high kinetic energy of about 10 eV.

Keywords: laser ablation plume, optical emission, graphite, diamond film

1. INTRODUCTION

Inorganic carbon materials such as diamond, diamond-like carbon (DLC), C_{60} fullerenes, and carbon nanotubes are very promising for electronics devices or mechanical applications. Especially, diamond thin films have potential applications as heat sink, hard coatings and wide-gap semiconductors owing to their superior properties.

So far, diamond thin films have been mostly synthesized by chemical vapor deposition (CVD) method in hydrogen-containing atmospheres [1-3]. Atomic hydrogen has been considered to have an important role on CVD diamond nucleation [4-7]. Recently, we have reported diamond nucleation and growth in a low-pressure hydrogen-free oxidizing environment by pulsed laser deposition (PLD) method [8]. PLD is a well-established technique for thin film preparation [9,10], and also has been applied to synthesis of carbon materials such as DLC films [11,12] and fullerenes [13] using a graphite target. Therefore, it is of great interest to understand the characteristics and dynamics of the species in the plasma plume generated during laser ablation of graphite. Optical emission spectroscopy (OES) is a powerful tool to assess information on the laser ablated species, their velocities, and their spatial distributions. While for laser ablation of graphite, the optical emission study in hydrogen [14], nitrogen [15,16], helium [17] and argon atmosphere [18] is well reported, there have been very few reports dealing with graphite ablation in oxygen gas atmosphere [19].

In order to understand the mechanism of diamond growth by PLD, we have carried out the spatially and time-resolved optical emission analysis of spectra and images of plasma plume recorded during the pulsed KrF excimer laser ablation of graphite in various oxygen pressures.

2. EXPERIMENTAL

The PLD apparatus and the optical emission measurement system are schematically shown in Fig. 1. After the PLD chamber was evacuated to less than 10^{-6} Torr, oxygen gas (99.999% purity) was fed into the chamber to oxygen pressure of 10^{-3} ~ 1 Torr through a mass flow controller or needle valve. A pulsed KrF excimer laser beam (wavelength; 248nm, pulse duration; 20ns) was introduced into the chamber through lens and quartz window. The laser beam was focused onto the polycrystalline graphite target (99.99% purity) with an incident angle of 45°, a repetition rate of 5 Hz, and the laser fluence of about 3×10^8 W/cm^2 on the target surface. The graphite target was rotated at approximately 8 rpm to avoid drilling. The substrate was placed on the substrate holder, parallel to the target and at about 2 cm away from the target surface. In this system, the pressure of the ambient gas and substrate temperature can be controlled.

Time-resolved images of the plasma plume were recorded by gated intensified-CCD (ICCD) system (Andor Co., Ltd.: DH510-18-F-01, minimum gate width of 5 ns) interlocking the laser pulse and gate of the intensifier by delay pulse generator (Stanford Research System Co., Ltd.: DG535) and personal computer. For the time-resolved imaging, CCD was placed in front of the window of chamber so that the entrance slit of CCD faced normal to the target-to-substrate direction. In case of the optical emission spectra measurement, the emission from the ablation plasma plume was focused by

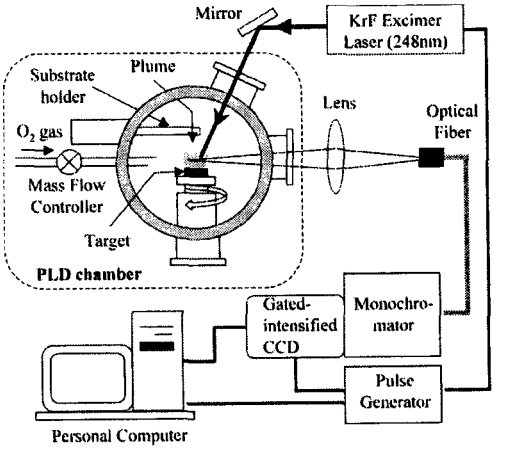

Figure 1. Schematic illustration of KrF excimer laser deposition chamber with an optical emission measurement system.

f = 330 mm focus lens on the entrance slit of a 127 mm monochromator (Oriel instruments Co., Ltd.: MS127i). After that, the spectra resolved optical emission from the plasma plume was detected by the CCD system. By moving the focus lens mechanically, we can obtain the spatially resolved optical emission spectra.

The substrates used in this work are single crystalline sapphire (0001) (α-Al_2O_3) substrates. By annealing the mechanochemically polished substrate, we can obtain the ultra-smooth substrate, which has atomic steps and atomically flat terraces [20]. This substrate was cleaned ultrasonically by acetone and ethanol before set in the PLD chamber with the substrate holder. The substrate was heated up to and kept at 550 °C during the film deposition. The deposited films were characterized by field emission scanning electron microscopy (FE-SEM) and micro Raman spectroscopy measurements.

3. RESULTS AND DISCUSSION

Fig. 2 shows time-integrated optical emission spectra of the plasma plume in high vacuum (~2×10^{-7} Torr) and ambient oxygen gas pressure of 0.15 and 5 Torr, respectively. These spectra were taken at a laser fluence of 3×10^8 W/cm^2 and a distance of 0.5 mm from the target surface. In high vacuum, the emission of C_2 Swan system (transition $d^3\Pi_g$- $a^3\Pi_u$, vibrant sequences Δv = 0, +1, +2) and the emission line from atomic and ionic carbon (CI, CII) are observed as shown in Fig. 2(a). In oxygen atmosphere, the spectra are dominated by Swan band emission of C_2 molecule and emission lines of C atom, (Fig. 2(b), (c)). It is also seen that the emission intensities of C_2 Swan band rapidly increase with oxygen pressure, in contrast with that of C atom. So far, the ambient gas pressure dependence of C_2 Swan band emission intensity has been reported for hydrogen and nitrogen atmospheres [14,16]. In both cases, the emission intensity of C_2 molecule increases with the increase in ambient gas pressure, which is consistent with our result.

The dependence of emission intensities of C atom (467.7nm) and C_2 molecule (479.3nm) on distance from the target in high vacuum and oxygen pressure of 0.15 and 5 Torr is shown in Fig. 3. We can see that the intensities of C atom decrease rapidly with distance from the target, and afterwards the emission lines disappear near the substrate surface in any oxygen pressures. The strongest emission of C atom is observed at oxygen pressure of 5 Torr, which extension is about 7 mm away from the target in our measurement system. On the other hand, the emission of C_2 molecule also decreases with distance and disappears near the substrate in both high vacuum and oxygen pressure of 5 Torr. But in oxygen pressure of 0.15 Torr, Swan band emission of C_2 molecule can be observed even near the substrate surface as shown in Fig. 3(b). It is noteworthy here that diamond nucleation and growth are observed under this oxygen pressure [8].

Fig. 4 shows the SEM photograph of the film deposited on the ultra-smooth sapphire substrate in oxygen gas pressure of 0.15 Torr (laser frequency of 5 Hz, fluence of 3×10^8 W/cm^2, 4 hours deposition). The inset in Fig. 4 shows the resultant micro Raman spectrum of the same film. From this spectrum, one can see a first-order diamond peak centered at 1332.8 cm^{-1} and full-width at

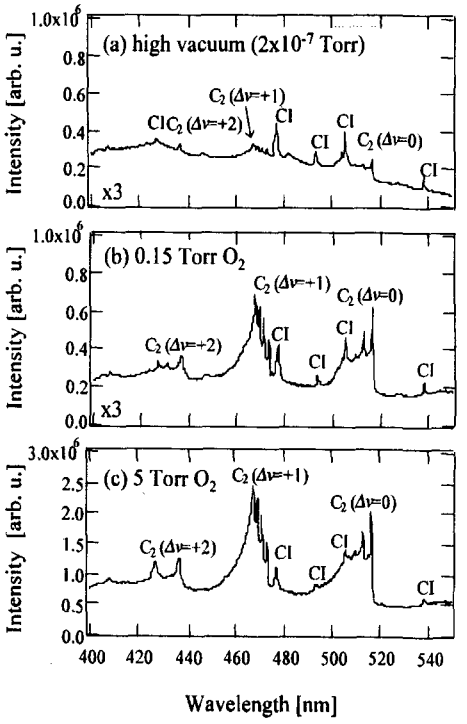

Figure 2. Time-integrated optical emission spectra during pulsed laser ablation of graphite in (a) high vacuum, (b) 0.15 Torr O_2 gas and (c) 5 Torr O_2 gas.

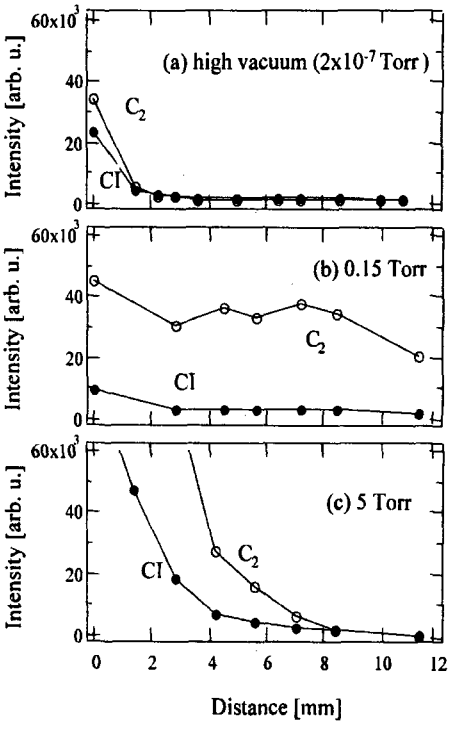

Figure 3. Dependence of C and C_2 emission intensities on distance from the target surface in (a) high vacuum, (b) 0.15 Torr O_2 gas and (c) 5 Torr O_2 gas

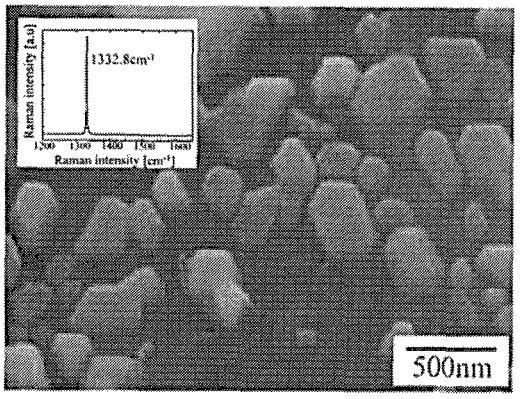

Figure 4. SEM image of the film deposited at 550 °C on the ultra-smooth sapphire (0001) substrate in 0.15 Torr O_2 gas. The inset shows micro Raman spectrum of the film.

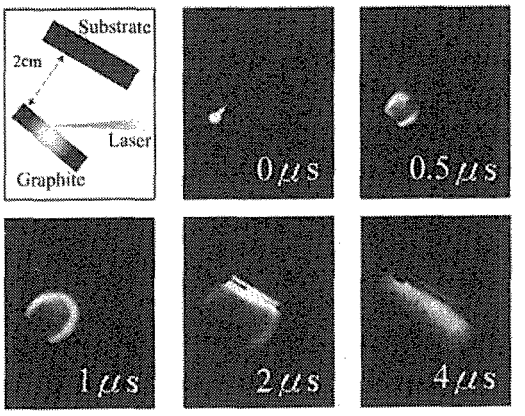

Figure 5. Time-resolved images of the plasma plume after one-shot pulsed laser ablation of graphite in 0.15 Torr O_2 gas.

half-maximum (FWHM) of 3.4 cm^{-1}. In other atmospheres such as high vacuum and oxygen pressure of 5 Torr, we did not observed the peaks originated from the diamond crystal in Raman spectroscopy. The film deposited in high vacuum was a black colored similar to graphitic or amorphous carbon, while no films were deposited in oxygen pressure of 5 Torr.

The time-resolved images of plasma plume in oxygen pressure of 0.15 Torr recorded at delay times between 0 μsec and 4 μs are shown in Fig. 5. "Time zero" means the moment just after the laser pulse impinged onto the graphite target. It is observed that the initial plume spreads out from the target surface emitting the visible light, afterwards the front edge of the plasma plume reaches the substrate surface at 2 μs after the laser pulse impinging. The time-resolved image at 4 μs also reveals that the plume reaching the substrate is reflected by the substrate. According to the spatial distribution measurement of emission intensities shown in Fig. 3, the emission observed near the substrate is that of C_2 molecule. From this result, emission near the substrate and that reflected by the substrate as shown in Fig. 5 is supposed to originate from C_2 molecule. The expansion velocity of the plume edge calculated from the images at 0 μs and 1 μs is estimated to be about 1.6×10^3 m/s, which corresponds to kinetic energy of approximately 10 eV. This indicates that the species with high kinetic energy, mainly C_2 molecule, collide with the substrate under the diamond film growth condition.

As reported earlier by us, diamond thin films can be synthesized in the oxygen pressure of 0.15 Torr. The emission of C_2 molecule can be observed near the substrate only in 0.15 Torr as shown in Fig. 3. Considering these results, it is possible that C_2 molecule, whose kinetic energy is as high as 10 eV, has an important role on diamond nucleation and growth of the present PLD process. In spite of the formation of C_2 molecule in other ambient gas species such as hydrogen or nitrogen [14-16], there has been no report of successful diamond synthesis by PLD in such atmospheres. Further investigations should be carried out to elucidate the dynamics in the plasma plume and to trace the reactions on the substrate surface for the diamond growth performed through a PLD method in the hydrogen-free oxidizing environment.

4. CONCLUSION

The optical emission study of the plasma plume generated by KrF excimer laser ablation of graphite in high vacuum and ambient oxygen gas has been carried out. The time-integrated emission spectra were dominated by emission of C_2 Swan band and emission lines of C atom. The intensity of C_2 Swan band emission increased with the oxygen pressure. From the spatially resolved intensity measurements, emission from C_2 molecule was observed even near the substrate surface in oxygen pressure of 0.15 Torr which suits diamond nucleation and growth proceeds. The time-resolved images indicated that the ejected species from the graphite target have high kinetic energy of about 10 eV and collide with the substrate surface and are then reflected.

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