Excimer laser ablation process characteristics for carbon nitride and diamond-like films preparation

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Abstract

We deposited diamond-like carbon (DLC) thin films and carbon nitride (CN) thin films by KrF excimer laser ablation of graphite carbon target in helium, hydrogen, nitrogen and mixed nitrogen and hydrogen gas ambient conditions. We report spectroscopic properties of the laser plasma plume produced during DLC and CN thin film deposition. Optical emission measurements at non-reactive helium ambient gas showed the appearance of neutral and ionic species such as C and C+ . Strong emission from molecules, CH, C2 and CN produced by the reaction in gaseous phase was observed with the ambient hydrogen and nitrogen gases. The properties of DLC and CN thin films are strongly affected by the laser plume dynamics. DLC and CN films were deposited on a quartz substrate and a single-crystalline Si(100) wafer at room temperature. Typical deposited DLC and CN thin films had an optical band gap of ~2.0 eV. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Diamond-like carbon

1. Introduction

The pulsed laser deposition (PLD) method has been used to produce thin films of a variety of materials such as diamond-like carbon (DLC), high temperature superconductors (HTS), semiconductors, ferroelectrics, nitride and metal compounds [1–6]. DLC films and carbon nitride (CN) films in particular are metastable amorphous materials which have been studied intensively both theoretically and experimentally due to their diamond-like properties such as hardness, highly optical transparency, chemical inertness and high resistivity [7,8]. Owing to their excellent properties, many opportunities for electronic applications have been expected [9]. For example, the DLC film is proposed as a material for field electron emitting devices.

PLD is rapidly proving to be an effective method for the preparation of various thin films. Despite its growing importance, the microscopic details of the processes responsible for some of the characteristic features of PLD are not well understood [10–13]. The congruent ablation of particles, plasma formation, and the interaction of the particles with ambient gas, are believed to be relevant in determining the film composition and structure.

In this study, we present optical emission spectroscopic studies on laser plasma plumes produced by KrF excimer laser ablation of graphite carbon target [14–20]. To prepare high quality DLC and CN thin films, we spectroscopically investigated a plasma plume generated by KrF laser ablation of a graphite target. We also investigated the optical absorption characteristics of the DLC and CN films prepared under various deposition conditions.

2. Experiment

Fig. 1 shows a schematic diagram of the PLD and the optical measurement systems used in this study. After a chamber (ø 300 mm) was exhausted by a turbo-molecular pump to a base pressure of 5×10−7 T, pure hydrogen gas, helium gas, nitrogen gas or a mixture of hydrogen and nitrogen gas was fed into the chamber. In the chamber, a graphite carbon target (99.999% purity, ø 30 mm) was mounted on the rocking holder. A KrF pulsed excimer laser beam (Lambda Physik Model LPX305icc, maximum energy 850 mJ, λ = 248 nm) was introduced into the chamber through lenses and a fused quartz window. The laser beam with a spot size of 1.8×2.8 mm2 impinges on the target at an incident angle of 45 or 90°. The maximum laser energy density on the target was estimated to be about 8 J/cm2. Spectral profiles (λ = 330–800 nm) and the temporal behavior of the luminous plasma plume at different conditions were measured by a scanning 250 mm-monochromator...
equipped with a photomultiplier and a digital oscilloscope. Emission light from the plasma plume at the distance of \( d = 0, 5, 10, 20, \) and \( 30 \) mm from the target surface was collected by a \( f = 300 \) mm convex lens and was focused on the entrance slit of the monochromator.

In order to prepare thin films, a quartz substrate and a single-crystalline Si(100) wafer were positioned \( 40 \) mm apart from the target surface at room temperature. DLC thin films were deposited by 12 000 laser shots in \( 100-800 \) mT ambient gas pressures. CN films were deposited by 18 000 laser shots in \( 100 \) mT partial pressure of ambient nitrogen gas. UV–visible light transparency and the optical band gap of the prepared DLC and CN films were measured by using a Shimadzu model UV-160 spectrophotometer, and IR absorption was investigated using a Fourier transform infrared spectrophotometer (Shimadzu model FTIR 8200A). Table 1 shows the deposition condition of thin films in this study.

### 3. Results and discussion

Fig. 2 shows the emission spectra from the plasma plumes in ultra-high vacuum (UHV) \( (~5 \times 10^{-7} \) T) and ambient helium gas pressures of 100 mT. At UHV, the spectrum originates almost from mono-atomic carbons (C) and a few carbon ions (C\(^+\)). In helium atmosphere emission lines C, C\(^+\) and helium ion (656.0 nm) were observed. Although both emission spectra look alike, there are some differences. The carbon atomic line at UHV changes to two ion lines at helium ambient conditions.

Fig. 3 shows the emission spectra from the plasma plumes observed at various distances from the target surface when the hydrogen gas pressure is 200 mT at a laser fluence of \( 4 \) J/cm\(^2\). In a hydrogen atmosphere, strong emission lines from neutral and ionic molecular species such as CH and C\(_2\) were observed. The spectral lines from carbon atoms and H\(_a\) (656.3 nm) were also identified. All the identified spectral lines of C\(_2\) molecular species are emitted from C\(_2\) Swan

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Deposition conditions of the DLC and CN thin films preparation</th>
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<tbody>
<tr>
<td><strong>DLC thin films</strong></td>
<td><strong>CN thin films</strong></td>
</tr>
<tr>
<td>Ambient gas</td>
<td>He</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>50–800 mT</td>
</tr>
<tr>
<td>Target</td>
<td>Graphite carbon target (purity 99.999%)</td>
</tr>
<tr>
<td>Fluence</td>
<td>4–8 J/cm(^2)</td>
</tr>
<tr>
<td>Number of laser pulses</td>
<td>9 000–36 000</td>
</tr>
<tr>
<td>Target–substrate distance</td>
<td>40 mm</td>
</tr>
<tr>
<td>Base pressure</td>
<td>( ~5 \times 10^{-7} ) T</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Substrate</td>
<td>Fused quartz</td>
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</tbody>
</table>

Fig. 1. Schematic of experimental setup for KrF excimer laser deposition of thin films and plasma plume optical measurement system.
Bands ($d^3Π_g \rightarrow a^3Π_u$). In the UHV, C and C$^+$ spectra were observed, but when hydrogen or nitrogen gas was introduced, the C and C$^+$ spectra were mostly hidden by the CH (430 nm) system and the C$_2$ spectra. The spectral intensity ratios of CH/C and CH/H$\alpha$ decrease rapidly over 20 mm from the target surface. Fig. 4 shows the electron density calculated from the Stark broadening of H$\alpha$ [20]. Electron density rapidly decreases between 10 and 20 mm. These results show that CH molecules seem to be formed by the reaction of emitted carbon atoms with excited hydrogen near the target surface.

Fig. 3. H$_2$ emission spectra of the plasma plumes at various distances from the target surface.

Fig. 5 shows typical optical emission spectra in the spectral range 330–600 nm recorded in the distance $d = 10$ mm at a fluence of 6 J/cm$^2$ and at different N$_2$ pressures 100 and 200 mT. Both spectra were dominated by the optical emission from the CN violet system and the N$_2$ second positive system. Three strong vibration sequences of CN were well observed. The identified spectral lines of CN and N$_2$ molecular species are emitted from the CN violet system ($B^2Σ^+ \rightarrow X^2Σ^+, Δ = -1, 0, +1$) (421.6, 388.3, 359.0 nm) and N$_2$ second positive system ($C^3Π_u \rightarrow B^3Π_g$), respectively. Although at 200 mT N$_2$, the C$_2$ Swan bands were
observed, at 100 mT N₂, the C₂ bands were hardly visible. Both the CN and the C₂ system intensities increased with N₂ ambient gas pressure.

In UHV and He ambient gas, which are non-reactive conditions, only C and C⁺ spectral lines were identified.

Under the reactive ambient gas conditions, optical emission was governed by molecular spectra such as C₂ and CH systems in H₂ ambient gas, whereas in N₂ ambient gas were dominated only by the CN system. This result seems to show that carbon atoms and ions ejected from the target surface react with reactive gas near the target surface to form C₂ by a three body reaction near the target surface as follows [7,21]:

\[ \text{C} + \text{C} + \text{M} \rightarrow \text{C}_2 + \text{M}. \]  

Further, in the case of the N₂ ambient gas, the conversion mechanism of C₂ radical to CN radical probably exists. As a result, optical emission intensity of the C₂ Swan system becomes small, and the CN violet system intensity inversely increases. Like the interaction between the pulsed laser beam and a target, the reaction between the ejected carbons and the ambient gas is a non-stationary state. The spatial density profile of the spectral lines and density of electrons and ions and their energy state are dominant parameters to clarify and affect the quality of films by the PLD process.

Fig. 4. Electron density at various distances from the target surface.

Fig. 5. Emission spectra of the plasma plume at various N₂ pressures.
We measured the optical transparency characteristics to obtain the optimum processing deposition conditions of the high quality DLC and CN thin films. Transparency in the UV region of films deposited at higher laser energy density is improved and this means an increase in optical band gap energy. As clearly seen from Fig. 6(a), the DLC films are almost transparent in the visible range. The Tauc plot in Fig. 6(b) shows that the DLC film deposited at 800 mT has an optical band gap energy of 2.0 eV, which is about half of that of a diamond. Optical gap characteristics of the DLC films could be improved by controlling the pressure of the ambient hydrogen gas.

Fig. 7(a) shows the optical transparency characteristics of the CN films. Fig. 7(b) shows the Tauc plots for the CN films deposited at various partial pressures of hydrogen. We used a mixture of hydrogen gas and nitrogen gas to improve
optical characteristics by investigating the effect of hydrogen in the DLC and CN thin films. In spite of low hydrogen partial pressure compared with the deposition condition of DLC thin films, the CN film deposited at a 100 mT N₂ partial pressure (50% H₂) has an optical band gap energy of 1.9 eV, whereas, the CN film even in the case of 3% H₂ has a band gap of 1.4 eV. This value of a band gap of 1.4 eV could not be obtained even for DLC film preparation using 100 mT of pure H₂ ambient gas.

The infrared (IR) absorption measurement was performed to study the ratio of two stretching modes: sp³ CH₂ (2925 cm⁻¹, asymmetrical) and sp² CH₂ (2950 cm⁻¹, olefinic). For FTIR characterization, the DLC films were deposited on the quartz substrate and the Si(100) wafer at room temperature and 800 mT ambient hydrogen gas pressure. We determined that the laser energy density of 8 J/cm² was the optimum parameter for high optical quality DLC films. We also carried out IR reflection measurements of the DLC films deposited on the Si (100) substrate in the wave number range of 2000–1300 cm⁻¹. The stretching mode of the C=C conjugated was not detected. These results suggest that carbon–carbon double molecular bond

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Fig. 7. Optical properties of the CN thin films prepared in ambient N₂ with various H₂ partial gas pressure. (a) Transparency of the CN films; (b) Tauc plot of transparencies in (a).
alkenes) does not appear abundantly at least in the thin films. Although the films deposited in high vacuum were opaque, having a smaller optical band gap energy and poor adhesion to the substrate, they were tough. Hydrogen atoms terminate the dangling bonds of the amorphous carbon so that the properties of the DLC films are improved. However, in IR reflection measurements of the CN films deposited on the Si (100) substrate in the wave number range of 2000–1300 cm$^{-1}$, the stretching mode of C≡N (1600 cm$^{-1}$) was observed. The result suggests that a C≡C double molecular bonds exist in CN thin films. The IR absorption measurements for the DLC and the CN films were performed to study chemical bonding. For FTIR characterization, the CN films were deposited on a Si(100) wafer at room temperature. A typical IR absorption spectra for the CN film at a fluence of 6 J/cm$^2$ is shown in Fig. 8. An absorption peak around 2200 cm$^{-1}$ seemed to be due to the C≡N stretching mode.

4. Conclusion

We have optically studied the dynamics of the plasma plume during preparation of DLC and CN thin films by the PLD method. It was found that carbon atoms and ions emitted from the target react with ambient gases of hydrogen and nitrogen. CH and CN molecules are formed in the gaseous phase. A mechanism for the conversion of the C$_2$ radical to the CN radical probably exists. It was found that the optical characteristics could be improved by using a mixture of hydrogen gas and nitrogen gas.

Acknowledgements

The authors thank Y. Yamagata and Y. Nishihara for useful discussions and gratefully acknowledge the contribution of T. Matsumoto of the Kyusyu Tokai University for his useful suggestions.

References


