PULSED LASER DEPOSITION OF CARBON NITRIDE THIN FILMS FROM GRAPHITE TARGETS

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Abstract—Carbon nitride thin films were synthesized on Si(100) substrates by a pulsed Nd:YAG laser deposition. The laser beam is incident on the high-purity graphite targets. The films are grown using an energy density 3.8 J cm⁻² at a laser repetition rate of 10 Hz. The nitrogen gas pressure in the chamber is 10.0 Pa. Morphology features of the films have been obtained by employing the technique of scanning electron microscopy. Auger electron spectroscopy has been used to obtain compositional information about the films. The N/C composition ratio was found to vary from zero to 0.32 depending on deposition conditions. IR absorption spectra show two characteristic bands: a broad band composed of the graphite G-band and disordered D-band of carbon, and another associated with C-N triple bonds. Raman spectra have also been used to characterize the films. © 1998 Elsevier Science Ltd. All rights reserved.

Key Words—A. Carbon composites, C. infrared spectroscopy, C. Raman spectroscopy, C. scanning electron spectroscopy (SEM).

1. INTRODUCTION

The hardest materials known are diamond and cubic boron nitride, with hardness values of around 100 and 50 GPa, respectively. Recent calculations by Liu and Cohen [1,2] suggested that a hypothetical material, β-C₃N₄, may be as hard as diamond. This produced a surge of activity in the synthesis of carbon nitride (hereafter referred to as CNₓ) thin films. Various CNₓ films have been prepared by different deposition techniques including reactive DC magnetron sputtering [3,4], RF sputtering [5–7], chemical vapor deposition [8,9], ion beam assisted deposition [10–12] and pulsed laser deposition (PLD) [13–17]. The synthesis of pure β-C₃N₄ remains an open challenge. In this paper we report our experimental results on synthesizing CNₓ films using pulsed laser deposition. All samples were analyzed by a field-emission secondary electron microscope (FE-SEM), Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy (FT-IR) and a micro-Raman spectrometer.

2. EXPERIMENTAL

The PLD apparatus used in these experiments is shown schematically in Fig. 1 [18]. A deposition chamber was evacuated by a turbo-molecular pump and a rotary pump. The laser used in the present study was a pulsed Nd:YAG laser (Lumonics YM600: wavelength of 532 nm, pulse duration of 6.5 ns, maximum output energy of 340 mJ). The laser beam was focused on the high purity (more than 99.999%) graphite targets at 45°, which were placed in the center of the stainless deposition chamber (Ø400 mm x 370 mm). The radiated area was kept at about 2.8 mm². The laser energy density was fixed at 3.8 J cm⁻². The targets were rotated at about 20 rpm to avoid pitting during the deposition. Single crystal Si(100) substrates of size approximately 4 cm² were ultrasonically cleaned in consecutive baths of ethanol and rinsed in high-purity deionized water prior to loading in the deposition chamber. Prior to actual deposition, the Si(100) substrates were cleaned in situ by reverse sputter-etching to remove any residual contamination. The Si(100) substrates were
located at a distance of 60 mm from the facing target and were heated up to 650°C by an IR lamp. The substrate temperature was measured by a thermocouple. The thermocouple was used as an input to a programmable temperature controller that drove the input power to the IR lamp. An external RF bias at 13.56 MHz or negative DC bias was applied to the substrate holder. The gas pressure was varied from a base pressure (below $4.0 \times 10^{-4}$ Pa) to 10.0 Pa (100% nitrogen). After 36,000–72,000 laser shots at 10 Hz repetition rate, the deposition process was completed. The film thickness was about 2000 Å and the deposition rate was about 33 Å min$^{-1}$ without bias voltage. Table 1 shows the deposition conditions for the preparation of CN$_x$ thin films.

The surface morphology was observed by a field-emission secondary electron microscope (FE-SEM: JEOL JSM-6300F). The composition and structure of the CN$_x$ films were examined by Auger electron spectroscopy (AES: JEOL JUMP-30), Fourier transform infrared spectroscopy (FT-IR: JEOL JIR-5500) and a micro-Raman spectrometer (Renishaw system 2000). The Raman spectra were obtained using an Ar$^+$ ion laser operated at 514.5 nm (2.41 eV) at a power of 40 mW.

3. RESULTS AND DISCUSSION

The surface morphology of the CN$_x$ films on the Si(100) substrate was examined by FE-SEM, as shown in Fig. 2. The film prepared at room temperature (Fig. 2(a)) is homogeneous with the occasional incorporation of spherical particles ejected from targets due to surface heating above the melting point, while the film prepared at 650°C (Fig. 2(b)) consists of many rugged particles of which sizes are about 50 nm.

AES analysis showed that the films are free (within the detection limit of this technique) from impurities and only signals from C and N are observed. Figure 3 shows the variation of the N/C composition ratio measured by AES in the films as a function of the substrate temperature $T_s$. An N/C composition ratio of 0.28 was found at room temperature. For the higher substrate temperatures, the N/C composition

<table>
<thead>
<tr>
<th>Laser</th>
<th>Pulsed Nd:YAG laser</th>
</tr>
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<tbody>
<tr>
<td>Wavelength</td>
<td>$\lambda = 532$ nm</td>
</tr>
<tr>
<td>Pulse width</td>
<td>$\tau = 6.5$ ns</td>
</tr>
<tr>
<td>Energy density</td>
<td>$E_d = 3.8$ J cm$^{-2}$</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Target</th>
<th>C (purity 99.9999%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotating speed of target</td>
<td>$\sim 20$ rpm</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si(100)</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>6.0 cm</td>
</tr>
<tr>
<td>Ultimate pressure</td>
<td>$&lt;4.0 \times 10^{-4}$ Pa</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>1.0–10.0 Pa (100% nitrogen)</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>$T_s =$ room temperature 650°C</td>
</tr>
<tr>
<td>DC bias voltage</td>
<td>$V_b =$ 0–$-150$ V</td>
</tr>
<tr>
<td>Deposition time</td>
<td>60–120 minutes</td>
</tr>
</tbody>
</table>

![100 nm](a) room temperature

![100 nm](b) 650°C

Fig. 2. FE-SEM micrographs of CN$_x$ films deposited on Si(100) at substrate temperatures of (a) room temperature and (b) 650°C ($P_{\text{total}} = 10.0$ Pa, $E_d = 3.8$ J cm$^{-2}$, $d = 6.0$ cm).

![Graph](Fig. 3. Variation of the N/C composition ratio as a function of the substrate temperature.)
Pulsed laser deposition of carbon nitride thin films from graphite targets

The following conclusions can be drawn from the results:

1. The N/C composition ratio is affected by the substrate temperature and reaches as much as 0.32.
2. Raman results show the presence of both disordered carbon (D-band) and graphitic sp²-bonded carbon (G-band).
3. FT-IR measurement indicates the presence of a C≡N triple bond.

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