Pulsed laser deposition of carbon nitride nanoparticles under a remote nitrogen plasma atmosphere: the role of nitrogen pressure and substrate temperature

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Abstract
Carbon nitride layers were deposited on a (100) Si substrate by CO$_2$ IR laser ablation of graphite in a remote nitrogen plasma atmosphere. Different diagnostic techniques such as X-ray photoelectron (XPS) and Raman spectroscopies, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to characterize the deposited layers as a function of nitrogen pressure ($P_{N_2}$) and substrate temperature ($T_s$). The deposits have a granular structure with a fairly rough surface as observed by SEM and AFM. Raman spectroscopy shows a change in the size of sp$^2$ carbon clusters domains (graphite-like structure) and gives an idea of the disorder in the deposit network. XPS analyses give evidence of a decrease in the sp$^2$ carbon atoms contribution with increasing $P_{N_2}$ in the 4-100 Pa range associated with the increase of the nitrogen concentration in the coatings.

Introduction
There has been a growing interest in the field of deposition and characterization of carbon nitride films due to their interesting characteristics and wide range of promising applications such as cutting tools, wear resistance and other optical and electrical properties. Since Cohen [1], who predicted the super hard compound B=C$_4$N$_4$, several papers have been published concerning the deposition of carbon nitride films. Pulsed Laser Deposition (PLD) has proved to be a promising and versatile technique, amongst many others in depositing a variety of materials, including carbon nitride layers. The laser wavelength used for ablation plays a dominant role in defining the characteristics and morphology of the deposited layers. The choice of the right wavelength and fluence helps to determine the surface morphology forming thin film or nanoparticles layer. The present article reports on the synthesis of carbon nitride CN$_x$ coatings by the reactive Pulsed Laser Deposition (PLD) technique. In this process, a Transversely Excited Atmospheric pressure (TEA) CO$_2$ laser ablation of a graphite target was used in a remote Nitrogen Plasma Afterglow (NPA). Reactions of ablated carbon
fragments with reactive nitrogen species present in the plasma afterglow lead to the formation of the coating on the substrate. In previous papers, results on the characterization of carbon nitride nanoparticles layers deposited using CO$_2$ IR laser [2] and on their composition determined by X-ray photoelectron spectroscopy [3] have been presented. In this work, the structural changes of the coatings as function of nitrogen pressure and substrate temperature are investigated.

**Experimental**

The experimental set up is schematically presented in figure 1. Carbon nitride layers were deposited on an oriented p-type doped silicon Si (100) substrate (99.999999 % purity) placed on in a plan parallel to that of the graphite target (99.95% purity) at a distance d = 0.02 m. Each substrate was cleaned using methanol and acetone in an ultra-sound bath for 3 min successively, then rinsed in deionized water for 1 min. The layers were deposited by ablation of a graphite target using an Infra-Red CO$_2$ ($\lambda$ = 10.6µm) pulsed laser (203 LUMONICS). The laser beam was focused on the target with an angle of 45°. The energy density of the laser pulse was about 1 J/cm$^2$ and 1800 laser pulses at a 1 Hz repetition rate were used. The nitrogen flow was excited in an electrode-less microwave discharge (2450 MHz) using a fixed transmitted microwave power energy of 1000 W. The NPA was fed into the reaction chamber located at a distance of 0.72 m far from the discharge zone by continuous pumping (rotary pump, 33 m$^3$/h$^1$). The initial base pressure of the system was about 7×10$^{-5}$ Pa. All substrates were pretreated by a NPA at a pressure of 1000 Pa in order to remove the adsorbed water vapor or oxygen trace from their surface and to improve the adhesion performance of the deposited layer.

![Diagram](image)

**Figure 1: Experimental set up of the CO$_2$ PLD carbon nitride coating deposition**

In our experimental conditions, the substrate was more or less subjected to the influence of the short-lived afterglow (see ref. 4) depending on the value of the nitrogen pressure (P$_{N2}$). Then, its temperature is closely dependent on this last parameter. In order to control the process, the substrate temperature was recorded using a thermocouple and it was ranging from 300 to 450 K, corresponding to pressures varying from 4 to 1000 Pa.

Different diagnostic techniques were used to characterize the deposited layers: XPS analyses were performed with a VG Escalab 220 XL spectrometer. The curve resolving procedure involved fitting the experimental spectra using Gaussian-Lorentzian components.
with no asymmetry except for the peak at 284.6 eV. Raman spectra were acquired on a LABRAM microspectrometer. The Raman spectra were recorded in the 150 cm\(^{-1}\) to 3500 cm\(^{-1}\) range. For analysis, the 800 to 1800 cm\(^{-1}\) region were fitted with two (Gaussian + Lorentzian) peaks centered at approximately 1570 cm\(^{-1}\) and 1350 cm\(^{-1}\). Fit parameters (height, width, position) were allowed to vary in order to get the best result. The surface morphology of the deposits was observed with the help of a LEO 982 ZEISS SEM at 30000 × magnification. The surface texture of the layers was characterized using tapping mode atomic force microscopy (TM AFM) for 1 × 1 \(\mu\)m\(^2\) scan size on a Nanoscope III instrument (version- 3.2) system.

Results and discussion

Effect of nitrogen pressure

- XPS characterization

Figure 2 shows the C 1s peaks of the CN\(_x\) coatings deposited under different nitrogen pressures with the substrate temperature varying between 300 to 450 K. The C 1s spectra are broad and asymmetric indicating the presence of several different types of carbon atoms bonds. It is possible to decompose the C 1s spectrum in at least six components as shown in figure 3. According to Jama et al. [3], the main peaks are assigned to different carbon environments. The first at 284.6 eV, taken as a BE reference, is attributed to graphitic carbon atoms. The second at 285.3 eV is a mixture of pure sp\(^3\) hybridized carbon C (sp\(^3\)), sp\(^2\) hybridized carbon and sp\(^3\) hybridized carbon with one nitrogen neighbor (N-C (sp\(^3\)) and N-C (sp\(^3\))). The third at 286.3 eV is due to C (sp\(^2\)) surrounded by two N atoms. The peaks at 286.9, 288.3 and 289.7 eV are respectively attributed to C (sp\(^3\)) surrounded by two, three and four N atoms. In the 4–100 Pa P\(_{N_2}\) range, a decrease in the sp\(^2\) carbon atoms contribution is associated with the increase of the nitrogen concentration in the coatings with increasing P\(_{N_2}\). For P\(_{N_2}\) equal to or higher than 700 Pa, an increase in sp\(^2\) carbon atoms contribution is observed, associated with a progressive

![Figure 2: C 1s peaks of the graphite target (a), PLD carbon (b) and PLD CN\(_x\) coatings deposited at different P\(_{N_2}\): (c: 4 Pa), (d: 100 Pa), (e: 300 Pa), (f: 500 Pa), (g: 700 Pa), (h: 1000 Pa).](image1)

![Figure 3: C1s peak decomposition of the PLD carbon nitride coating deposited under nitrogen pressure of 100 Pa (substrate temperature = 350 K).](image2)
graphitization of the CNₙ coatings.

**SEM and AFM Results**

SEM and AFM analyses showed that the deposits have a granular structure with a fairly rough surface. It is clearly visible, as shown in figure 4, that the surface is totally covered by sub-micronic particles, the average particle diameter ranging between 50 and 200 nm. These particles coalesce into several hundreds of nanometer in diameter cauliflower-like grains, with an inhomogeneous distribution all over the surface. By increasing the nitrogen pressure, the size of the cauliflower-like grains increases inducing an increase in the layer porosity.

The topography of the layers was also observed by atomic force microscopy (AFM). Three dimensions (3D) of 1 × 1 µm² scan size show that the surface topography of the layers is fairly rough, and is composed of connected islands having an inhomogeneous sizes, suggesting that the carbon nitride layer nucleates in a three-dimensional island growth mode as shown in figure 5. As the nitrogen pressure increases from 100 to 700 Pa, the size of the islands becomes larger and they are more inhomogeneous. AFM measurements of the peak-to-valley height for one island give a maximum value of several hundreds of nm. It was found that the average of measured root-mean-square (rms) surface roughness increased from 55 to 100 nm upon raising the nitrogen pressure from 100 to 700 Pa.

![Figure 4: SEM image at 30000 x magnification of the coating deposited at nitrogen pressure of 300 Pa (substrate temperature = 400 K).](image)

![Figure 5: (3D) AFM image of the coating deposited at nitrogen pressure of 300 Pa.](image)

**Raman spectroscopy**

The Raman spectra of the deposited coatings consist of two features: a G peak at around 1570 cm⁻¹ and a D peak at around 1350 cm⁻¹. The G peak arises from symmetric vibrations and originates from the optical zone center (E₂g mode) of perfect graphite crystal [5]. The D peak, which is correlated to the in-plane vibrational modes at the surface of the sp² carbon domains, originates from a zone-edge (A₁g mode) which is activated by disorder [5]. A higher intensity of the D peak by comparison to the G peak intensity is observed. An additional broad band centered at 700 cm⁻¹, characteristic of the out-of-plane bending mode of graphite-like domain [6], is also detected. The intensity I_D/I_G ratio, full width at half maximum of the G peak (Γ_G), D and G positions and nitrogen content in percentage in layer as function of the nitrogen...
pressure are presented in Table I. A shift in the D peak position towards low wavenumbers when increasing the nitrogen pressure from 4 to 700 Pa is observed. It can be explained by the increase of the C-N bonding concentration in a tetrahedral configuration. Moreover, a decrease of the \( I_D/I_G \) ratio and an increase of the \( G \) peak width \( \Gamma_G \) when increasing the nitrogen pressure are also observed. These evolutions could be due to a change in the \( \text{sp}^2 \) clusters domain sizes [7] and thus the decrease of the ratio \( I_D/I_G \) ratio may signify an increase of the cluster size which is coherent with the results evidenced from MEB and AFM analyses. The increase of \( \Gamma_G \) along with the decrease of the \( I_D/I_G \) ratio indicates also a decrease of the network disorder.

<table>
<thead>
<tr>
<th>Pressure (Pa)</th>
<th>Nitrogen content (atomic %)</th>
<th>D-Position (cm(^{-1}))</th>
<th>G-Position (cm(^{-1}))</th>
<th>( \Gamma_G ) (cm(^{-1}))</th>
<th>( I_D/I_G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>without ( N_2 )</td>
<td>2.3 %</td>
<td>1364.4</td>
<td>1564.7</td>
<td>130.5</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>15.5 %</td>
<td>1352.9</td>
<td>1572.8</td>
<td>133.6</td>
<td>4.7</td>
</tr>
<tr>
<td>100</td>
<td>30.3 %</td>
<td>1350.1</td>
<td>1571.0</td>
<td>137.1</td>
<td>4.2</td>
</tr>
<tr>
<td>300</td>
<td>33.5 %</td>
<td>1351.9</td>
<td>1570.3</td>
<td>144.5</td>
<td>4.3</td>
</tr>
<tr>
<td>700</td>
<td>34.6 %</td>
<td>1345.8</td>
<td>1568.9</td>
<td>155.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

**Table I: Composition and Raman parameters for the CNx layers deposited at different nitrogen pressures (substrate temperature between 300 to 450 K)**

**Effect of substrate temperature:**

The effect of substrate temperature on the physical and structural properties of the deposited layers is investigated in the range of 350 – 625 K. It is found upon increasing the temperature that no significant changes are observed. SEM and AFM images show that the deposit is composed of cauliflower-like sub-micronic particles with no dependence on the substrate temperature. The surface roughness is about 60 nm except at 625 K, where it is equal to 45 nm. Raman analyses also show no changes in the \( I_D/I_G \) ratio, \( \Gamma_G \), \( G \) positions or in nitrogen concentration in the layers, as a function of the substrate temperature. However, a slight shift in the D peak position towards the low wavenumbers is observed. The results are listed in Table II as function of the substrate temperature.

**Table II: Composition as determined by XPS and Raman parameters for the CNx layers deposited at different substrate temperatures (\( P_{\text{\( N_2 \)}} = 100 \) Pa)**
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Nitrogen content (atomic %)</th>
<th>D-Position (cm⁻¹)</th>
<th>G-Position (cm⁻¹)</th>
<th>$\Gamma_C$ (cm⁻¹)</th>
<th>$I_D/I_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>25.1 %</td>
<td>1355.0</td>
<td>1566.8</td>
<td>143.0</td>
<td>4.1</td>
</tr>
<tr>
<td>425</td>
<td>25.5 %</td>
<td>1352.1</td>
<td>1568.3</td>
<td>141.5</td>
<td>4.0</td>
</tr>
<tr>
<td>475</td>
<td>26.1 %</td>
<td>1348.5</td>
<td>1568.6</td>
<td>142.0</td>
<td>4.0</td>
</tr>
<tr>
<td>525</td>
<td>25.3 %</td>
<td>1347.2</td>
<td>1570.2</td>
<td>140.7</td>
<td>4.0</td>
</tr>
<tr>
<td>575</td>
<td>27.5 %</td>
<td>1345.4</td>
<td>1569.8</td>
<td>140.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Conclusion**

Laser ablation of graphite under nitrogen plasma allows the deposition of CN₅ layers. In this work several analytical and diagnostic tools were used to characterize the effect of nitrogen pressure and substrate temperature on the structure of carbon nitride layers. No significant changes were observed by changing the substrate temperature in the range of 350 – 575 K. However, an increase in the sp³-cluster size and a decrease of the network disorder when increasing the nitrogen pressure was suggested from Raman results. Such increase in the sp³ carbon cluster size is also consistent with the increase of the cauliflower-grain size evidenced from SEM and AFM. XPS analyses showed an increase in the sp³ carbon atoms contribution with increasing Pₙ₂ in the 4 -100 Pa range. For Pₙ₂ equal to or higher than 700 Pa an increase in sp³ carbon atoms contribution is observed, associated with a progressive graphitization of the CN₅ coatings.

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**References**