

INFLUENCE OF SUBSTRATE TEMPERATURE ON AMORPHOUS CARBON AND AMORPHOUS CARBON NITRIDE: A COMPARATIVE STUDY

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Abstract We have studied the influence of the substrate temperature (ST) on the structural properties of the amorphous carbon (a-C) films and amorphous carbon nitride (a-CN_x) films deposited by Xe-Cl excimer pulsed laser deposition (PLD) using camphoric carbon (CC) target. The a-C and a-CN_x films are deposited with varying ST range from 20 to 500 °C. To incorporate nitrogen in the film, we have introduced nitrogen gas (N₂) at 0.8 Torr in the PLD chamber. The effects of the ST and ambient N pressure on the surface morphology, composition and structural properties of the films have been investigated using SEM, AFM, XPS, Raman and FTIR spectroscopy. The amorphous structure of a-C and a-CN_x films are found can be changed by ST and the ratio of sp² trigonal component to sp³ tetrahedral component is strongly dependent on the ST and N gas ambient.

Keywords: amorphous carbon, amorphous carbon nitride, substrate temperature and pulsed laser deposition.

1. INTRODUCTION

Amorphous carbon (a-C) films have been drawing research interest for the past decades due to its wealth of atomic structure and properties. A-C films are technologically important materials that are used as optically transparent films and abrasion-resistant coatings. The wide spectrum of the atomic structures and properties of a-C films stems from the capability of C to form different hybridizations. Depending on the short-range environment, physical and mechanical properties of a-C films can vary between the two crystalline extreme of C, i.e., graphite and diamond. The physical properties responsible for this versatility are related to the relative amount of sp¹, sp² and sp³ hybridized bonds and the atomic connectivity within the film [1]. Changes in deposition temperature are expected to produce changes in the sp²/sp³ bond ratio and the amount of free volume in the films. Moreover, since the properties of a-C films were revealed to mainly depend on the ratio of sp²/sp³ carbon bonds, and in order to investigate the factors that influence the change of sp²/sp³ ratio, the deposition of a-C films on quartz and silicon (100) substrates by excimer laser beams using CC target with varying ST from 20 to 500 °C has been carried out. We also have introduced N into the chamber to deposit the N incorporated carbonaceous films.

Amorphous carbon nitride films (a-CN_x x: N to C ratio) is an interesting material and has been widely investigated in the past decade since Liu and Cohen [2] reported that metastable crystalline - C₃N₄, might possess hardness comparable to that of diamond, and also because of the possible applications of this material as magnetic media coatings and as semiconductor. It has been found that a-CN_x films also have a low friction coefficient, chemical inertness, and variable optical band gap [3]. Till now, in most deposited a-CN_x films, the atomic ratio of N/C is much lower than the N/C ratio in the perfect - C₃N₄ material. Furthermore, it has been reported [4] that although - C₃N₄ forms in very small crystallites that are embedded in amorphous sp²-bonded carbon nitride, most deposited carbon nitride films are composed of many types of bonds between C and N. Hard films require sp³-C in the C₃N₄ network, while sp²-C in C₃N₄ network will result in much softer materials. It is known that, at high ST sp³-C transforms into sp²-C and N incorporation in the films become difficult. On the other hand, high ST is needed for the formation of crystalline phase and low ST will cause amorphous structure of the films. Therefore, it is necessary to optimize the ST in order to achieve high x, which will ensure the stable C-N bonds and avoid graphite-like a-CN_x in the films. In order to improve the properties of a-CN_x films for practical applications, details studies of the microstructure of a-CN_x films are

necessary. Because the microstructure of a-C and a-CN_x films are strongly dependent on the deposition conditions, in this work, we will discuss the different bonding structure that occur in a-CN_x films when they are deposited at different ST and compared with a-C films which were also deposited in the same range of the corresponding ST. The objective of this study is to develop improved procedures for characterizing a-C and a-CN_x films.

2. EXPERIMENTAL

In this paper, we report the effects of the ST from 20 to 500^oC and ambient N pressure at 0.8 Torr on the deposition of a-CN_x films by PLD compared with a-C films, which were also deposited in the same range of the corresponding ST. For a-CN_x films, the CC target was ablated by pulsed XeCl excimer laser under N gas ambient, which operates at a wavelength of 308 nm for 900 laser shots on quartz and silicon (100) substrates. At a repetition rate of 2 Hz, the laser beam of 0.15 J average pulse energy and 20 ns pulse width was focused at a 45 degrees angle onto a target by a ultraviolet grade plano-convex lens. The laser fluence was maintained at 1.8 to 2.2 J/cm² by adjusting the lens to target distance. The substrate was mounted on a metal substrate stage holder parallel to the CC target at a distance of 45 mm. In order to ensure a uniform ablation rate, the CC target was rotate at each 50 shots. The deposition chamber was evacuated to a base pressure approximately at 2 x 10⁻⁵ Torr using a turbomolecular pump. The ST was first raised to 500^oC for 2 min before deposition in order to sublimate surface oxides formed after etching treatment. After that, N gas was allowed until the chamber pressure

is at 0.8 Torr. While for a-C films, the CC target also was ablated in the same range of ST using the above procedure without N gas ambient. The surface orphology, composition and structural properties of the deposited a-C and a-CN_x films have been investigated using Scanning electron microscopy (SEM), Atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (Raman).

3. RESULTS AND DISCUSSIONS

3.1. Thickness and deposition rate

The film thickness and average deposition rate of a-C and a-CN_x films deposited at 20^oC was about 170 to 180 nm and 0.19 to 0.2 nm per pulse, and 150 to 160 nm and 0.17 to 0.18 nm per pulse, respectively. Both the film thickness and average deposition rate of a-C and a-CN_x films are exponentially decreases with the increase of ST.

3.2. SEM and AFM morphology

SEM and AFM showed that, the surface morphology of a-CN_x film deposited at 20^oC was very smooth and has only a few feature compared with the a-C film at the same ST. The particle size and roughness of a-CN_x films are significantly changed with the ST and a few small particles appeared at 200^oC. The particle size and roughness increased with the increasing of ST. It was found that, above 400^oC the particle size rapidly increased while the density of the particles and the surface roughness obviously decreased, which is implies that some small particles have merged into a large particle due to the enhance surface migration of the

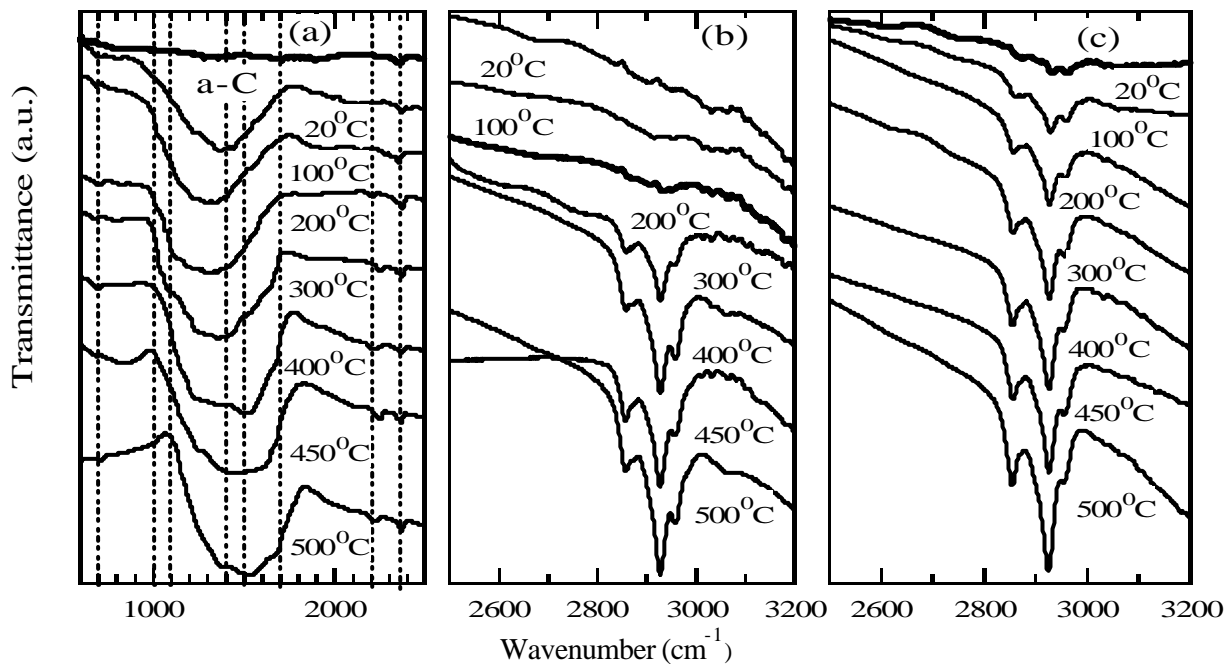


Fig. 1. FTIR spectra obtained from (a) Typical a-C and a-CN_x, (b) a-C, and (c) a-CN_x films deposited at various substrate temperature.

deposited CC species. For a-C films, the particle size and surface roughness almost unchanged up to 200 and linearly increases thereafter with ST.

3.3. FTIR spectroscopy

FTIR transmittance spectra were measured in the wave number range from 600 to 3200 cm^{-1} (Fig. 1). It has been reported that, FTIR absorption for C-H stretching vibrations on $\text{sp}^2\text{-C}$ is found in the 2950 to 3060 cm^{-1} range, while for $\text{sp}^3\text{-C}$ in the range 2850-2945 cm^{-1} range [5] and the peaks around 2926 and 2956 cm^{-1} are the most prominent, assigned to $-\text{CH}_2\text{sp}^3$ asymmetric and $-\text{CH}_2\text{sp}^2$ olefinic bonds respectively, and the peaks around 2855 cm^{-1} indicate the formation of sp^3 bonding [6]. It is clear from the spectra (Fig. 1 (a) and (b)) that as ST increases the three characteristic peaks of diamond like carbon [7] peaks in the region 2850 to 3000 cm^{-1} become more and more prominent suggest the formation of crystalline structure in the films. Should be noted here that the increasing peaks degree of a- CN_x film is higher than a-C film. The absence of clear appearance of peaks in the a-C up to 200 $^\circ\text{C}$ suggests the amorphous nature of the films. This is in good agreement with the Raman spectrum of the film at the same ST. Figure 1 (c) shows band 1 at around 700 cm^{-1} is due to the out-of-plane bending mode for the graphite-like domain [8]. Broad absorption band 2 at 1000 to 1700 cm^{-1} indicates that the films structure is predominantly amorphous with $\text{sp}^2\text{-C}$ vibration modes, and is related to Raman active D and G modes[9]. Band 3 at 1100 to 1400 cm^{-1} and band 4 at 1500 to 1700 cm^{-1} and band 5 at around 2200 cm^{-1} are due to C-N, C=C and/or C=N and C-N stretching vibration modes, respectively [10]. In our spectra, bands 3, 4 and 5 are very weak and as ST is increased, starting from around 200 $^\circ\text{C}$ the broad absorption band 2 becomes narrow and although small, the intensity of band 3, 4 and 5 increase gradually up to 400 $^\circ\text{C}$ and

decrease thereafter. This indicate the components of the C-N, C=N, C=C and C-N bonds increases with the ST up to 400 $^\circ\text{C}$ and decrease thereafter, which is also confirmed by the XPS analyses. The broad band between 1000 and 1700 cm^{-1} and the band centered at 2200 cm^{-1} do not appear in a-C. The absorption peak at around 2350 cm^{-1} , which is observed in a-C and a- CN_x films, can be attributed to the CO_2 stretching mode arising from oxygen contamination at the film surface [11].

3.4. XPS spectroscopy

The bonding state and chemical composition in the aC and a CN_x films were analyzed using XPS after the 0.5 keV Ar⁺ ion etching of film surface for 3 min. The C 1s peak position of a-C film is found to be almost unchanged up to 200 $^\circ\text{C}$ at about 284.8 eV (Fig. 2a), which is 1.0 eV lower than that of diamond at 285.8 eV. With the increase in ST higher than 200 $^\circ\text{C}$, the C 1s peak becomes narrow and gradually shifts toward lower binding energy and approaches the binding energy of graphite at 284.25 eV [12] when ST reaches 500 $^\circ\text{C}$. For a- CN_x film at 20 $^\circ\text{C}$, the C 1s peak position is decreased to 284.4 eV compared to a-C film at the same ST, may be due to the formation of C-N bond. With the increase in ST, the C 1s peak (Fig. 2a) becomes narrow and the N 1s peak (Fig. 2b) splits into two subpeaks indicating the enhancement degree of crystallization in the films. Further, as ST increases, the C 1s peak shifts toward lower binding energy and approaches the binding energy of graphite at 284.25 eV [12] when ST reaches 400 $^\circ\text{C}$. This shift can be explained as the bonding state of the films changes from low diamond like sp^3 bonding to graphite like sp^2

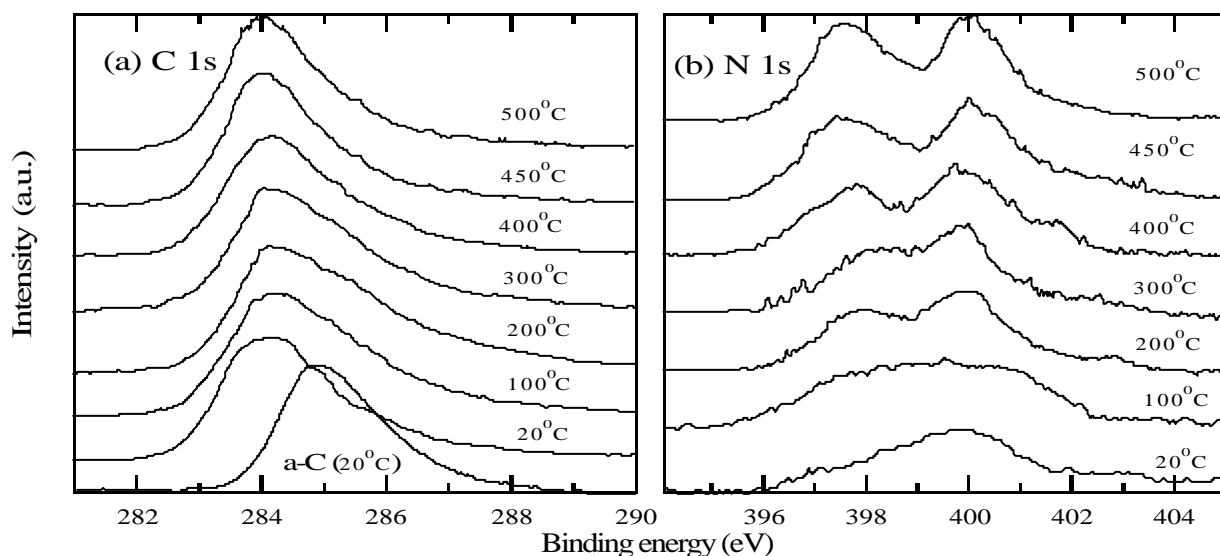


Fig. 2. Influence of the substrate temperature on: (a) the C 1s of a-C and a- CN_x , and (b) the N 1s core level spectra of a- CN_x films.

bonding with the increase in ST. On the other hand, the N 1s peak spectra showed asymmetric bands centered at around 400 eV. With the increases of the ST up to 200 °C, the N 1s spectrum splits into two bands located at around 400 eV and 398 eV. It implies a change in bonding structure. The N signal of the film deposited at 400 °C can be deconvoluted (not shown) into two peaks at 398.4 and 400.5 eV. The chemical shift of 2.1 eV between these two components reflects two different binding states of N, which can be attributed to

N-C and N=C [13]. Thus, the observed chemical shift indicates that N atoms are bound to the C atoms. The N/C ratio in the film is found to increase gradually from 3.69 % to 15.05 %, with an increase in the ST up to 400 °C, hereafter it decrease at higher ST (Fig. 3a). With the increase in ST, the surface migration of C and N species will be enhanced, which will accelerate the chemical reaction between C and N and consequently improve the N content. However, at ST of higher than 400 °C, N content in the films decreases because the stable C-N bonding only remains since the volatile bonding decomposes and N molecules released from the films.

3.5. Raman spectroscopy

Raman spectroscopy is a suitable tool for the analysis of carbon and carbon related materials. The a-CN_x films spectra showed a broad asymmetric band at 1000 to 1700 cm⁻¹, which is similar to the a-C films. The broad bands were deconvoluted using Gaussian line shapes into D and G peaks (not shown), responsible for the disordered sp²-C induced by the linking with sp³-C atoms and the graphitic phase, respectively. The intensity ratio of the D to G band (I_D/I_G) of a-C film is gradually increases with ST. The I_D/I_G of a-CN_x film is higher than a-C film at 20 °C, and increases with ST till 400 °C after which it increases rapidly (Fig. 3a). Since the high relative intensity of I_D/I_G is preferred to synthesize -C₃N₄ [14], these results indicate that high ST is favorable to C₃N₄ structure and is in agreement with the XPS results. Both, Raman D and G peaks of a-C film are not much changed with ST up to 200 °C after which it gradually increases with higher ST. For a-CN_x film, Raman D and G peaks are upshifted with N incorporation at 20 °C. Raman D peak is not much changed with ST, while Raman G peak slowly shifts upward up to 400 °C and then rapidly shifts afterwards (Fig. 3b). The results indicate that sp² fraction increases with N incorporation at 20 °C and gradually increases with ST till 400 °C after which it increases rapidly with further increase of ST. An increasing in sp² bonding in these films resulted in a G peak shift to a higher wave number. Raman linewidth (FWHM) of D and G peaks of a-C film almost unchanged with ST up to 200 °C after which it gradually decreases with higher ST. For a-CN_x film, Raman FWHM of D and G peaks decreases with N

at 20 °C and keep decreasing slightly with ST (Fig. 3c), indicating better quality of the a-CN_x films. This shows that N incorporation causes an increase in the number and size of the graphitic domains in the films. Furthermore, we also observed a very weak N-C peak for the sample at around 2100 cm⁻¹ [15], which implying

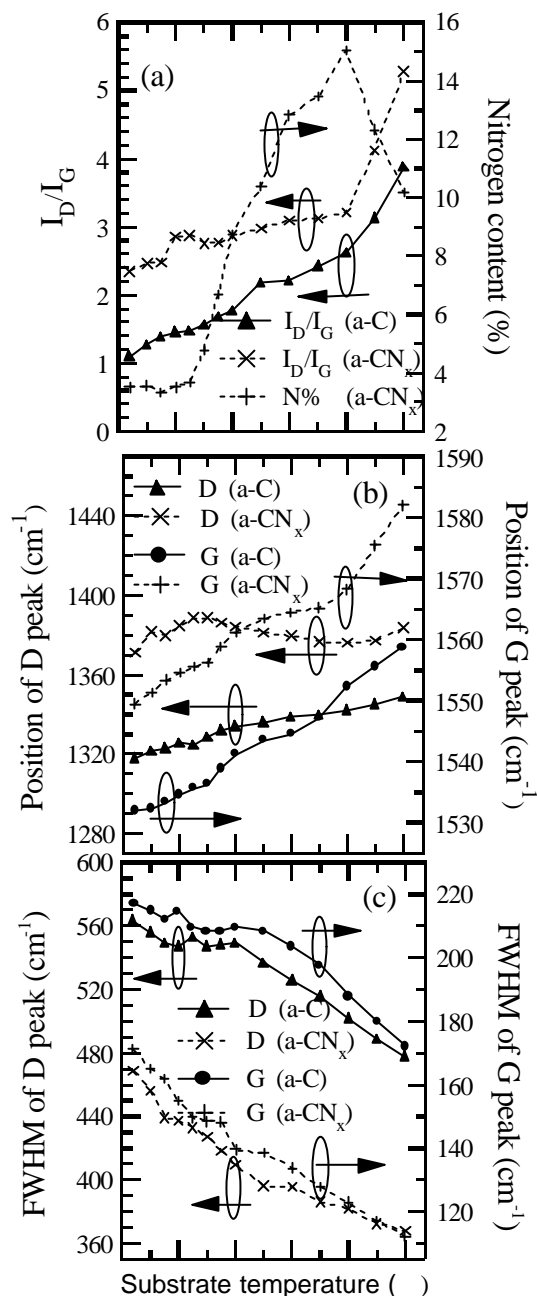


Fig. 3. Influence of the substrate temperature on: (a) the intensity ratio I_D/I_G and nitrogen content, (b) the position of D and G peaks, and (c) the FWHM of the D and G peaks.

very weak bonding. Both sp² and sp³ hybridized C atoms can be bonded to the N atoms in the deposited films, as revealed by the XPS, FTIR characterizations and has been confirmed by Raman spectroscopy.

4. CONCLUSIONS

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A-CN_x films have been deposited by excimer laser beams using CC target at 0.8 Torr N gas ambient with varying the ST from 20 to 500 °C and compared with a-C films, which were also deposited in the same range of the corresponding ST without N gas ambient. The dependence of the ST and N gas ambient on the surface morphology, composition and structural properties of the films was investigated. The particle size and roughness of a-C film are increased with ST. Whereas for a-CN_x films the particle size is increased rapidly, while the roughness is increased up to 400 and decreased afterwards with the ST. The N content increases with ST and reached its maximum value of 15.05 % at 400 °C and decreases afterwards. It was found that the amorphous structure of a-C and a-CN_x films can be changed by ST and the ratio of sp² trigonal component to sp³ tetrahedral component is strongly dependent on the ST and N gas ambient.

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