

X-ray Photoelectron Spectroscopy Analysis on the Bonding Properties of Amorphous Carbon Nitride Films

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Amorphous carbon nitride films (a-CN_x) were deposited by pulsed laser deposition (PLD) of camphoric carbon (CC) target at various substrate temperatures (ST). In this paper, the influence of ST on the synthesis of a-CN_x films is investigated. The nitrogen to carbon (N/C) atomic ratio and oxygen to carbon (O/C) atomic ratio, bonding state, and microstructure of the deposited a-CN_x films were characterized by X-ray photoelectron spectroscopy and were confirmed by other standard measurement techniques. The bonding states between the C and N and C and O in the deposited films are found to be significantly influenced by the ST during deposition process. The N/C and O/C atomic ratio of the a-CN_x films reached a maximum value of 15.05 at% and 10.2% at 400°C, respectively. The ST of 400°C was proposed to promote the desired sp³-hybridized C and C₃N₄ phase. The C-N bonding of C-N, C=N and C≡N were observed in the deposited a-CN_x films. Key words: PLD, substrate temperature, camphoric carbon, XPS, a-CN_x

1. INTRODUCTION

The a-CN_x film is expected to be an interesting new material because it exhibits outstanding properties, such as high value of hardness, low friction, chemical inertness, and variable electrical conductivity and optical band gap [1]. The local structural property that distinguishes potentially superhard and dense C₃N₄ structures from low-density and softer material is a C coordination, where hard materials require sp³-C in the C₃N₄ network, while sp²-C will lead to much softer materials [2].

The relative content of the C coordination is sensitive to deposition parameters such as substrate temperature (ST) of pulsed laser deposition (PLD). It is known that high ST will result in sp³-C transforming into sp²-C, i.e. graphitization, in the preparation of diamond-like C (DLC) films and also CN films [3]. The most important aspects of the characterization of CN films are to determine the bonding state, that is whether the bonding is single, double, or triple, and to evaluate the N:C ratio in each phase present [4]. X-ray photoelectron spectroscopy (XPS) analysis has been used for both purposes by a number of researchers [5,6].

2. EXPERIMENTAL PROCEDURE

Nitrogen gas was introduced at 0.8 Torr into the chamber to deposit N-incorporated carbonaceous films on quartz and silicon substrates by PLD using camphoric C (CC) target. The CC target was ablated by PLD (NISSIN 10X, λ = 308 nm, τ = 20 nsec, 2 Hz, 900 shots, 2.2 J/cm²). The substrate was mounted on a metal substrate stage holder parallel to the CC target at a distance of 45 mm. The deposition chamber was evacuated to a base pressure approximately 2 x

10⁻⁵ Torr using a turbomolecular pump.

In this paper, we present the composition, chemical bonding, and structure of the a-CN_x films deposited by PLD at various ST in range from 25 to 500°C characterized by XPS. A reference sample of amorphous C (a-C) film (Sample A) was also deposited without N gas ambient.

3. RESULTS AND DISCUSSION

The chemical composition and bonding state in the a-CN_x films were analyzed using XPS after the 0.5 keV Ar⁺ ion etching of film surface for 3 min. The chemical composition of the deposited films can be obtained according to oxygen to C (O/C) and the N to C atomic ratio (N/C). The N/C and O/C content in the films were evaluated using $N/C = (A_N/1.68) / (A_C/1.00)$ and $O/C = (A_O/2.49) / (A_C/1.00)$ where A_N, A_O, and A_C are the areas under the N 1s, O 1s, and C 1s core level spectra, and the constants of 1.68, 2.49, and 1.00 are the atomic sensitivity factors of N, O, and C, respectively.

The N/C ratio in the film was about 3.69 atomic percentage (at%) at 25°C and increased gradually, with an increase in the ST up to about 15.05 at% at 400°C, but it decreased at the ST higher than 400°C up to about 10.19 at% at 500°C (Fig. 1 left axis). With the increase in ST, the surface migration of C and N species would be enhanced, which would accelerate the chemical reaction between C and N and consequently improve the N content. However, at the ST higher than 400°C, N content in the film would decrease because the stable C-N bonding would remain, while the volatile bonding would be decomposed, resulting in N molecules being released from the films [3]. The increase of N content in the film

might also be explained due the fact that the lower deposition rate induced by ST corresponded to the lower C/N arriving ratio. Therefore, the higher N/C ratio in the a-CN_x films. Thus, the C to N species on the substrate surface is considered to determine the final N/C atomic ratio in the a-CN_x films within this range of ST (up to 400°C).

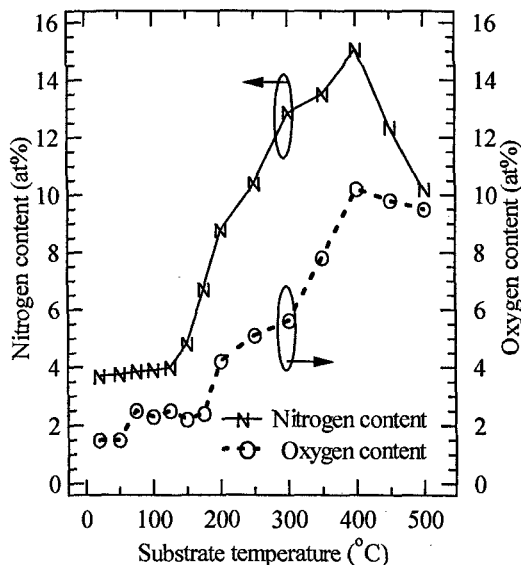


Fig. 1. Variation of (a) nitrogen (left-axis) and oxygen (right-axis) content with various substrate temperatures. (Left axis: N for nitrogen content. Right axis: O for oxygen content)

Furthermore, the increase of ST leads to an increase of C atom mobility. Some weak bonding, such as nitrile and other interstitial species, may become volatile and are detached from the film, which results in a decrease in the N/C ratio in the deposited films (over 400°C). In addition, the high desorption rate of CN and CNH species from the growth surface and the lower incorporation of volatile C-N species at elevated temperatures due to their low temperature of sublimation may also contribute to the low N/C ratio in deposited films [7]. The decrease of N content with the increase of ST (over 400°C) also may be due to the chemical sputtering effect. The sputtering rate of N in a thin film is much higher than that in C [8].

However, our result has shown the preferential sputtering of N should be responsible for the reduction of N content incorporated in the a-CN_x films deposited at higher ST (over 400°C). We also suggest that, with an increase of ST up to 400°C, 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 the ST higher than 400°C, N content in the film decreases because only the stable C-N bonding will remain since the volatile bonding decomposes and N molecules are released from the films [3].

It is well known that for the deposition of DLC

films, for temperatures higher than about 200°C, the surface mobility is sufficient for forming the more energetically favorable graphitic structure, over the amorphous phase found at lower temperatures [9]. Therefore, when depositing a-CN_x films above this temperature, we can assume that N atoms, and possibly also -C≡N molecules, will diffuse on the deposition surface until they either become bound in a low-energy lattice site, or react with other particles to form volatile molecules which can desorb. At higher temperatures the diffusion rate becomes higher, so more reactions are likely to take place. Furthermore, due to surface mobility, we can assume that C diffusion becomes more prevalent at higher temperatures, so N from the subsurface region could diffuse toward the surface, and there they recombine or react and are eventually desorbed.

Therefore, these can explain how we found the reduced N incorporation with increasing ST over 400°C. The desorption of N₂ suppresses N incorporation, while the desorption of C-containing species will involve the surface reaction process [10]. Pure C is unlikely to be desorbed since that would require physical sputtering, but C₂N₂ and to some extent also other CN species, can be expected to be involved. The formation of these volatile molecules can happen in many ways. It is likely that first -C≡N dimers are formed, either by dissociation of C₂N₂⁺ ions at impact at the deposition surface, or by reactions between C and N on the film surface. The formation of C₂N₂ molecules can result in a lower total N concentration in the a-CN_x films deposited at higher ST over 400°C. This type of chemical sputtering process would also result in a reduced deposition rate, especially at elevated ST [10].

An overview of XPS spectra of the deposited films indicates the presence of a very small O 1s content, in addition to the C and N constituents. The presence of O is probably related to the incorporation of O due to prolonged exposure of the samples to the experimental atmosphere before XPS measurements and accidental incorporation during deposition. In addition to C and N, O/C was detected at less than 1.5 at% as a minor contamination (superficial) for the sample A and a-CN_x samples deposited at 20°C that containing N/C = 3.69 at%. As shown in Fig. 1 (right axis), it was found that as the ST is increased from 25 through 400 to 500°C, the O content in the a-CN_x films increases from 1.5 at% through 10.2 at% and decreases to 9.5 at%, respectively.

The reason for the increased amount of O/C and N/C in the films with higher ST can be found in the porosity and low density of the a-CN_x material [11]. However, it should be noted that the presence of N in the C networks and oxygen due to minor contamination may also increase the electro-negativity of the a-CN_x compounds. As a result, with an increase of ST up to 400°C, the N content in the a-CN_x films reached a maximum value,

while the deposited films showed more polarity and tended to absorb the H₂O molecules present in the experimental atmosphere, and therefore the amount of O increased in the a-CN_x films. With further increase of ST up to 500°C, the decrease of N content in the a-CN_x films caused the decrease of electro-negativity and polarity of deposited films. As a result, the O content in the a-CN_x films decreased in ST over 400°C.

The variation of XPS C 1s core-level spectra of the a-CN_x films deposited at different ST is shown in Fig. 2. In general, one can clearly see that the full width at half maximum (FWHM) is broad and the spectrum profile is asymmetrical for the C 1s spectra taken for all the a-CN_x films prepared under different ST, indicating that the C atoms in the films are in different bonding configurations. The FWHM of XPS C 1s spectrum of sample A was about 1.7 eV and exhibited a narrow and regular shape. While the XPS C 1s spectra of a-CN_x films showed broad and asymmetric, which is enveloped at the higher binding energy side. We found that the FWHM of XPS spectra of a-CN_x films increased from about 1.7 to 3.1 eV as ST increased from 25 to 500°C, implying the degree of asymmetry increased in ST.

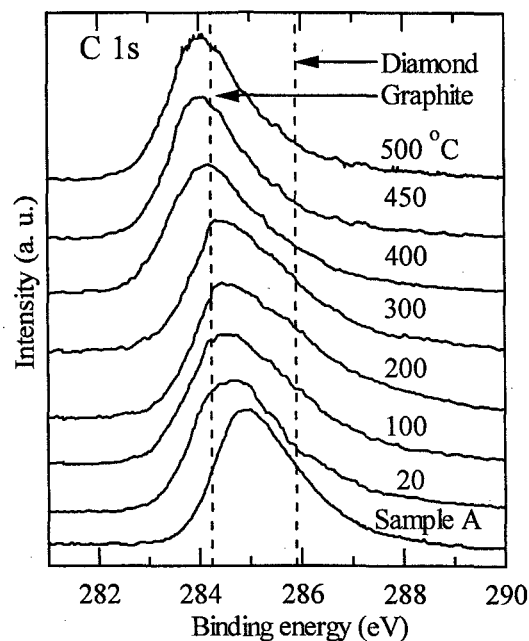


Fig. 2. Variation of XPS C 1s core level spectra of sample A, and a-CN_x films deposited at different substrate temperatures.

This suggests that there are several bonding configurations related to C atoms in the films. This effect is a clear indication that N atoms are involved in chemical bonds with C in three possible distinct chemical states: C-N, C=N, and C≡N bonds. The C 1s peak position of sample A is at 284.8 eV, which is 1.0 eV lower than that of diamond at 285.8 eV [12]. For a-CN_x film at 25 °C, C 1s peak position is decreased to 284.4 eV. This new peak suggests that a C-N bond has occurred. As ST increases, the C 1s peak shifts toward lower binding energy. When the ST reaches 400°C, the peak position approaches the binding energy of graphite at 284.25 eV [13]. It

can be explained that this shift is the change in the bonding state of the films from low diamond-like sp³ tetrahedral bonding to graphite-like sp² trihedral bonding with the increase in ST. The influence of the ST on the chemical status of the a-CN_x films is quite obvious.

The variation of XPS N 1s core-level spectra of the a-CN_x films deposited at different ST is shown in Fig. 3. The XPS N 1s spectra showed asymmetric broad peak centered at around 400 eV, corresponding to some bonding configurations related to N atoms. With the increase in ST, the N 1s peak splits into two subpeaks, which indicates that the degree of crystallization in the films is enhanced. We did not find any shift of the N 1s peak with increased of ST. However, as the ST increases to 200°C, the N 1s spectrum splits into two obvious bands that are located at around 400 and 398 eV. This implies a change in bonding structure, which occurred with increased of ST, i.e., the increase of ST has an obvious effect on the bonding of C and N atoms during thin film deposition.

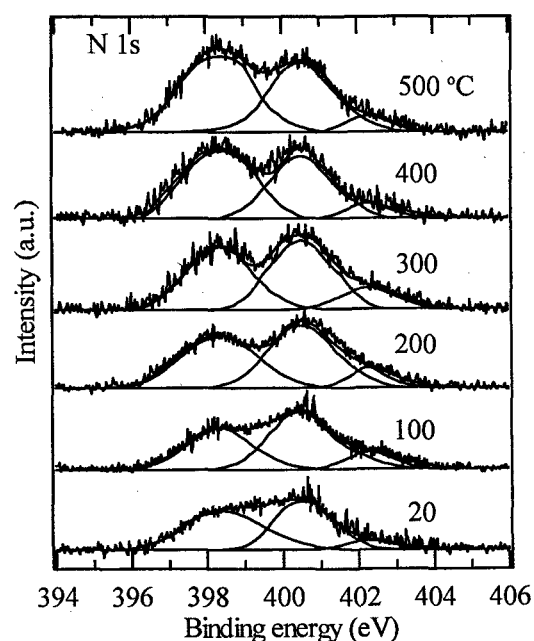


Fig. 3. Variation of XPS N 1s core level spectra of a-CN_x films deposited at different substrate temperatures, and their image of deconvolution of 3 peaks Gaussian line shape.

In order to give further evaluation of the bonding state and composition of the deposited films as a function of ST, an image of the possible chemical bonds of N in the films has been inferred from the deconvolution of the individual N 1s (Fig. 3) spectra of the films deposited at 20, 100, 200, 300, 400, and 500°C into 3 peaks Gaussian line shape. [5].

The best fits to XPS N 1s resulted in three Gaussian peaks. Peak 1 at the binding energy of 398.4eV is assigned to the sp³ tetrahedral C-N bonding with N being sp³ hybridization, while

peak 2 at 400.5 eV is assigned to the sp^2 trihedral C-N bonding with C_3N to C_2N stoichiometry. The chemical shift of 2.1 eV between these two components reflects two different bonding states of N, which can be attributed to $N\equiv C$ and $N=C$ [14]. Thus, the observed chemical shift indicates that N atoms are bound to the C atoms. Peak 3 at 402.3 eV is related to the N-O bonding that exists from O contamination at the film surface of the $a-CN_x$ films due to the high reactivity between N and O.

Figure 4 (left-axis) shows the P_1/P_2 peak area ratio varied with ST. The P_1/P_2 increased with increasing ST accompanied with an increase of N content up to 400 °C, after which both P_1/P_2 and N content in the films decreased. The P_1/P_2 value was approximately 1.25 for the $a-CN_x$ film deposited at 25°C and approximately 1.7 and 1.4 for the film deposited at 400 and 500°C, respectively. Fig. 4 (right axis) shows the variations of the N bonded to sp^3C and sp^2C content as a function of ST. The increase of the N- sp^3C content with ST is observed up to 400°C, and decreased thereafter. On the other hand, the N- sp^2C gradually increased up to 400°C, and increased with higher ST.

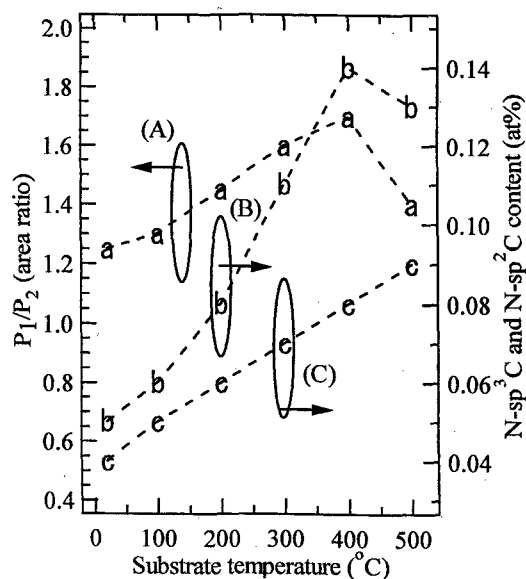


Fig. 4. P_1/P_2 peak ratio (left axis), N- sp^3C (right-axis), and N- sp^2C (right axis) content as a function of substrate temperatures. (Left axis: (A) for P_1/P_2 . Right axis: (B) for N- sp^3C , and (C) for N- sp^2C .)

These data indicate that N atoms bonded to the C atom in the graphite structure (N- sp^2C) are increase with higher ST. On the other hand, pentagons, which are promoted by incorporated N atoms, are unstable in the graphite structure and graphitized by ST above 400°C, accompanied with elimination of N atoms. Simultaneously, transformation of sp^3C atoms, which cross-linked between the graphite planes to sp^2C , takes place. These data may indicate that N atoms bonded to sp^3C are referentially removed by higher ST over 400°C.

4. CONCLUSIONS

The chemical compositional and structural modifications of $a-CN_x$ films deposited by PLD of CC target with varying ST under fixed low N partial pressure were studied. According to XPS measurements, the N/C ratio of the deposited $a-CN_x$ films can reach a value of 15.05% as ST reaches 400°C, and decreases with higher ST. It can be concluded that the reduction of N content and changes in bonding structure of N atoms in the $a-CN_x$ films by ST are caused by graphitization. The ST of 400°C was proposed to promote the desired sp^3C and the C_3N_4 phase. C and N species in the deposited films form stable bonds instead of a simple mixture. The chemical environments of the C and N species in the deposited films are strongly influenced by the ST during deposition. The bonding state between the C and N, and C and O in the deposited films, are found significantly influenced by the ST during deposition process. The C-N bonding of C-N, C=N and C≡N were observed in the $a-CN_x$ films.

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