

Raman scattering analysis of amorphous carbon nitride thin films prepared by pulsed laser deposition at various temperatures

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Raman scattering analysis revealed that the structure of carbon (C) films prepared by pulsed laser deposition at room temperature is predominantly amorphous and the structure of amorphous C nitride (a-CN_x) films can be changed with varying substrate temperatures (ST) from 25 to 500°C. The deposited a-CN_x films are composed of C-N and C≡N bonded materials, and the C-N and C≡N bonds are increased with ST. We have found no other obvious peaks can be distinguished in the range 900 to 2300 cm⁻¹ in which several peaks always appear in a-CN_x films. The spectra were deconvoluted into Raman D and G peaks and the structural parameters are determined. The upward shifts of Raman G peak towards 1592 cm⁻¹ shows the evidence of a progressive formation of crystallites in a-CN_x films upon increase of ST. While, the upward shifts of Raman D peak towards 1397 cm⁻¹ have been related to the decreased of bond-angle disorder and sp³ tetrahedral bonding in its structure. Raman FWHM and I_D/I_G also indicate that N incorporation with increased of ST caused an increase in the number and/or size of graphitic domains in the a-CN_x films.

Key words: Pulsed laser deposition, Substrate temperature, Camphoric carbon, Visible Raman, a-CN_x

1. INTRODUCTION

The structural characterization of amorphous carbon nitride (a-CN_x) films are complicated, because there is a variety of bonding configurations in carbon (C) and nitrogen (N) system. Investigation of structural modification induced due to effects of substrate temperature (ST) during pulsed laser deposition (PLD) process is important and meaningful in order to realize the structure and improve the properties of a-CN_x.

Raman spectra (RS) provide a wide range of structural and phase disorder information [1]. Raman spectroscopy is a suitable tool and a widely used technique to study the vibrational properties, and for the characterization and analysis of the macroscopic bonding structure of C and C related materials [2]. Visible Raman spectroscopy is a good probe to investigate the sp² configurations in C materials. RS of the two crystalline forms of C, graphite and diamond are well known. The first order RS consist of a single sharp line at about 1332 cm⁻¹ for diamond and at about 1350 cm⁻¹ (D peak) for polycrystalline graphite due to grain boundary effect, while another peak appears at about 1580 cm⁻¹ (known as G peak) for single crystal graphite results from the Raman allowed E_{2g} mode [3]. In this paper, the effect of ST on the deposition of a-CN_x films by PLD is studied in order to understand the structure and improve the properties of a-CN_x films for various practical applications.

2. EXPERIMENTAL

It is reported that the various properties of C films not only depend on their methods and

condition of deposition but also on the starting precursor materials. Till date, mostly graphite is being used as a solid target in sputtering, laser ablation, etc. for the preparation of C thin films. Camphor (C₁₀H₁₆O), a new C precursor, and a natural source, has both sp²-C and sp³-C while graphite is pure C has only sp²-C. The camphoric C (CC) target was ablated by PLD, operates at a wavelength of 308 nm for 900 laser shots. At a repetition rate of 2 Hz and 20 ns pulse width was focused at a 45° angle onto a target normal by ultraviolet grade plano-convex lens. The laser fluence was maintained in range from 1.8 to 2.2 J/cm² by adjusting the laser energy and the lens to target distance for adjusting the laser spot size.

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 at 2 x 10⁻⁵ Torr using a turbomolecular pump. After that N gas ambient was allowed until the chamber pressure is allayed at 0.8 Torr. To investigate the effects of ST on the structural properties of a-CN_x films, the CC target was ablated using the above procedure and ST was set in range from 25 to 500°C at 0.8 Torr of N gas ambient. The reference sample of a-C film (Sample A) has also been prepared using the above procedure at RT (25°C), without N gas ambient. The systematic variations of microstructure properties of the deposited films are studied through Raman scattering measurement are presented.

3. RESULTS AND DISCUSSIONS

RS were measured at room temperature (RT) using 488 nm line of Ar⁺ laser operating at a

power of 200 mW, while it was about 5 mW at the sample. Figure 1 displays the evolution of the RS in the range 800 to 2500 cm^{-1} of Sample A and a-CN_x films deposited at 25–500°C, respectively. The RS are vertically displaced for clarity, but otherwise displayed using the same scale. The Sample A exhibited a relatively symmetric broad band nearly at around 1545 cm^{-1} . While, the RS of the a-CN_x film deposited at 25°C had a broad asymmetric band at 1000 to 1700 cm^{-1} , which is almost similar to those of diamond-like C (DLC) films and to the Raman spectrum of Sample A deposited at the same ST.

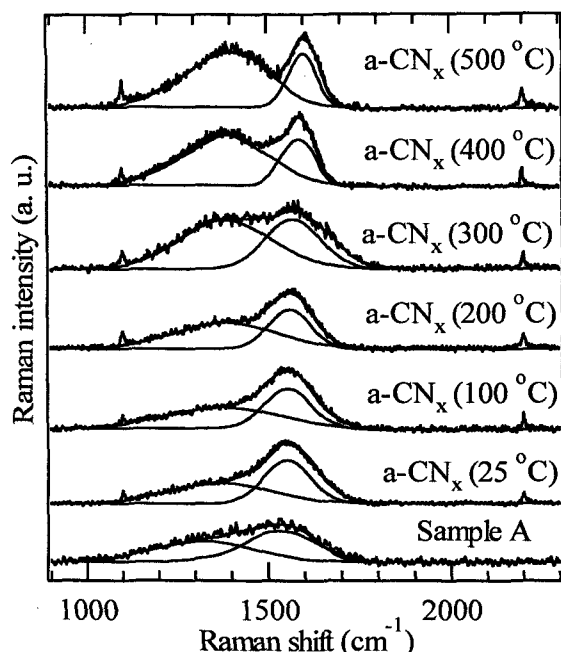


Fig. 1: Raman spectra of sample A, and a-CN_x films deposited by Method 1, and their image of deconvolution of Raman D and G peaks using 2 peaks Gaussian lines.

This indicated that the films had mainly a diamond-like structure. The broadband shapes of these films suggest that its structure is amorphous. The RS of Sample A and a-CN_x films deposited at 25°C reveal amorphous nature [4] of the deposited film from CC target. The strict selection rules for electronic transition set by the long-range translational symmetry of the crystal lattice are relaxed in amorphous state and therefore, more modes can contribute to Raman scattering resulting in the broadened Raman spectrum [4]. It has been postulated that a visible Raman spectrum with a relatively symmetrical G peak corresponds to high quality of DLC film, i.e. with high sp^3/sp^2 ratio.

It is clear that the broad band (peak at around 1545 cm^{-1}) resulted from the a-CN_x film gradually split into two peaks (Raman D and G peaks) with the increase of ST, may be due to the progressive crystallization upon increase of ST [4]. The RS indicate that a-CN_x films have a graphitic structure. The variation in the position and shape of these peaks are due to the structural changes, formation of disorder, polymer rings,

micro-graphite, etc., and in all cases the peaks between 1300–1400 cm^{-1} and 1500–1600 cm^{-1} are taken as evidence for the presence of a DLC in the films [5]. As shown in figure 1, upon careful investigation, we also have found a very weak Raman band peak at around 1100 cm^{-1} , that can be seen for all of a-CN_x films, which is can be considered due to the characteristic of C–N stretch (C–N single bond) [6] implying a very weak bonding. The development of C–N sp^3 bonds in a-CN_x films at increased ST may also suggests that the N content in the a-CN_x films increased with ST. As can be seen from Figure 1, we also found a very weak Raman band peak at around 2200 cm^{-1} , that can be seen for all a-CN_x films, which is characteristic of C–N stretch and assigned a very weak bonding, implying that the amount of the bonds was very small as compared to the other C–N bonding states. The Raman peak found here corresponds to the $\text{C}\equiv\text{N}$ bond stretching modes [7]. These observations agree to some extent, with the paracyanogen-like, $(\text{CN})_n$ structure proposed by Cuomo et al. [8] who have analyzed a-CN_x films deposited by reactive rf sputtering of C in N. They [8] have reported that the $\text{C}\equiv\text{N}$ are thought to be extremely stable due to one of the highest bond dissociation energies.

The experimental data were best fitted by two peaks considering Gaussian line shapes into two Raman bands of D and G peaks, and the linear background and the plot of RS for the Sample A and a-CN_x films in the range of 900 to 2300 cm^{-1} are shown in figure 1. As can be seen from figures, our experimental result shows that according to ST, Raman D peak intensity increases (Fig. 1) and Raman D and G peak positions shift to high wave number (Fig. 3). The upward shifting of the Raman G peak position (Fig. 4 (right-axis)) together with the increase of Raman D peak intensity (Fig. 1) is exactly the same trend as that observed from graphitization of CN films [9] and C films [10]. This phenomenon may reflect to the progress of graphitization of a-CN_x films because Raman D peak is assigned to sp^2 -C in which seems to be aromatic in structure.

Both, Raman D and G peaks of a-CN_x films are upward shifted with N incorporation initially at 25°C, compared to Sample A. This implies the a-CN_x films are dominated by sp^2 rather than sp^3 at 25°C and which might cause the crystallites to have a bigger size. Raman D peak is gradually increases with ST, while Raman G peak slowly shift upwards up to 400°C and then rapidly shift afterwards as shown in figure 4 (right-axis), which shows evidence of a formation of crystallites in a-CN_x films at higher ST. The results indicate that sp^2 fraction increases with N incorporation at 25°C and gradually increases with ST till 400°C, after which it increases rapidly with further increase of ST. An increasing in sp^2 bonding in these films resulted in a Raman G peak shift to a higher wave number [11].

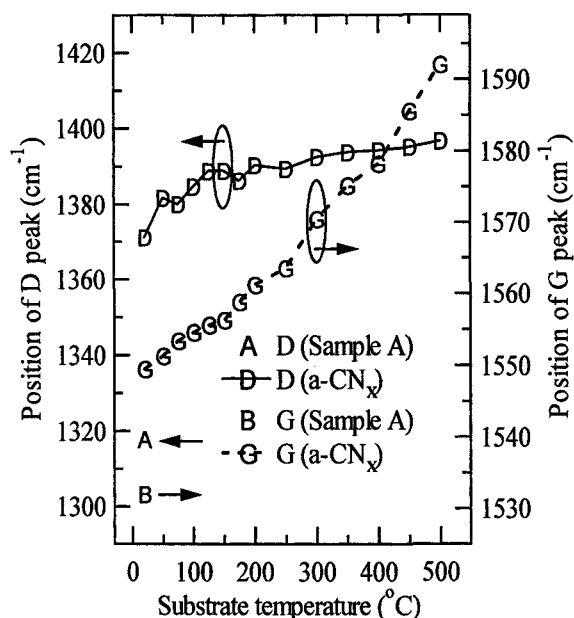


Fig. 2: Raman D (left-axis) and G (right-axis) peak positions of Sample A, and a-CN_x films as a function of substrate temperatures. (Left-axis: A for Sample A, and D for a-CN_x films. Right-axis: B for Sample A, and G for a-CN_x films).

As shown in figure 2 (left-axis), we have observed a transition point of an upward shift of the D peak at 100 and 400°C. We found that the D peak can be divided into three linear regions in the ST range of 20°C ≤ ST ≤ 100°C, 100°C ≤ ST ≤ 400°C and 400°C ≤ ST ≤ 500°C, which indicate domination of the structural modification of the a-CN_x films. Figure 2 (right-axis) shows the shift of the G peak from about 1370 to 1397 cm⁻¹, indicates the formation of disordered nano-crystalline graphite particles, upon increase of ST. The upward shift of Raman G peak towards higher frequency above 1580±5 cm⁻¹, implies that the a-CN_x films deposited at above 350°C are dominated by sp² trihedral bonding rather than sp³ tetrahedral bonding and the crystallites have a very small grain size [12]. According to our observations, the upward shift of D and G peaks in a-CN_x films upon increase of ST is due to the change of bond angle disorder up to 400°C and upward shift of D peak with rapidly upward shift of G peak at above 400°C, is due to the change in bonding (sp³/sp²) which in turn affects the structure of the a-CN_x films.

The sp² structure acts as a conduction part of the amorphous network [13], and the graphitic C formation is due to the presence of the sp² structure [14]. The upward shift of the Raman D and G peaks (Fig. 2) from their respective principle values of 1355 and 1580 cm⁻¹ of crystalline graphite phase with increase of ST indicate the presence of the bond angle disorder [12]. The upward shift of the G peak from about 1550 to 1590 cm⁻¹ indicates the formation of disordered nano-crystalline graphite particles [12] upon increase of ST. Such a shift of D and G peaks indicate that incorporation of N with

increases of ST causes progressive graphitization in the a-CN_x films. This may suggest that the increase of ST promotes the formation of sp²N-C or sp²C-C bonding.

The Raman FWHM of G peak is related to the bond angle disorder at sp² sites in the C system [4]. The gradual narrowing of the G peak indicates the development of long-range order in the a-CN_x films or disordering of the graphitic structure. The variation of Raman FWHM of D and G peaks as a function of ST is shown in figure 4. It is clear that the Raman FWHM of D and G peaks decreases significantly upon increase of ST, which indicates the increases of the crystallinity [15].

Raman FWHM of D and G peaks of a-CN_x films are decreases with N at 25°C compared to Sample A and keep decreasing slightly with ST, indicating better quality of the a-CN_x films. The decrease of Raman FWHM at the beginning clearly shows that the crystallinity in the film has increased with N incorporation at 25°C. Furthermore, a decrease in Raman FWHM afterwards shows an increase in crystallinity with further rise in ST and N incorporation. This shows that N incorporation causes an increase in the number and size of the graphitic domains in the films.

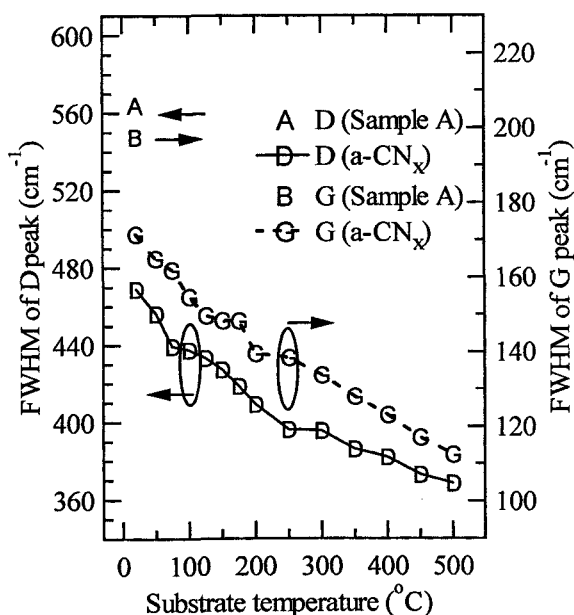


Fig. 3: Raman FWHM of D (left-axis) and G (right-axis) peaks of Sample A, and a-CN_x films deposited by Method 1 as a function of substrate temperatures. (Left-axis: A for Sample A, and D for a-CN_x films. Right-axis: B for Sample A, and G for a-CN_x films).

It was obvious that the increase in ST reduced the Raman FWHM of D and G peaks (Fig. 3). The narrowing of G peak with the increase in ST suggested the increase in graphitization in the C-C phase of the deposited films, which was similar to that in DLC films. The Raman D and G peaks shift to a higher frequency and the decrease of Raman FWHM of D and G peaks showed that

the N incorporation in a-CN_x films with increasing the ST favor the formation of sp² units. Beeman et al. [16] has reported the upward shifting of D peak increases the broadening and integral density of D peaks and therefore increases the intensity ratio of Raman I_D/I_G. The Raman I_D/I_G ratio (Fig. 4) of a-CN_x film (2.35) is found higher than Sample A (1.11) film at 25°C, rapidly increases from 2.35 to 2.86 with increasing of ST up to 100°C and gradually increases up to 3.22 at 400°C, which reflected the fact that the degree of disorder increased in the films. Raman I_D/I_G increases rapidly with further increase in ST over 400°C up to 5.27 at 500°C. The Raman I_D/I_G reflects the number and/or size of graphitic domains for a-C materials [4].

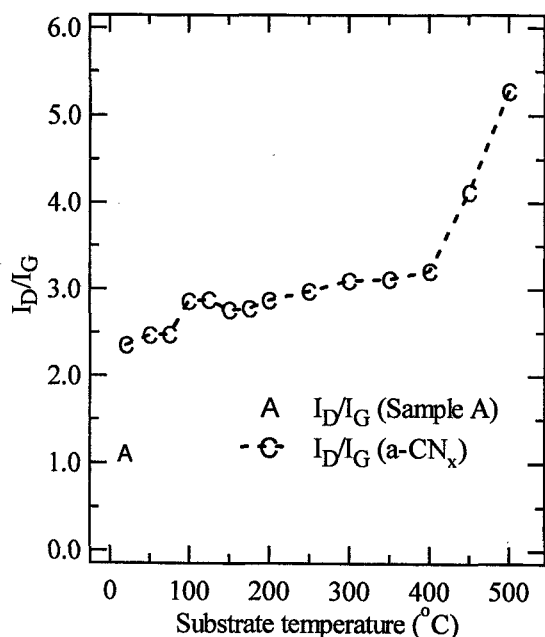


Fig. 4: Raman I_D/I_G of D and G peaks of Sample A, and a-CN_x films deposited by Method 1 as a function of substrate temperatures. (Left-axis: A for Sample A, and C for a-CN_x films).

We found the increased of Raman D and G peak and the Raman I_G/I_G, and the decreased of Raman FWHM with the increased of ST, which may indicate that N incorporation caused an increase in the number and/or size of graphitic domains in the a-CN_x films. Simultaneously, transformation of C atoms from sp³- to sp²-hybridization takes place. These results support the theoretical model of Beeman et al. [16] where they have predicted downshift of G peak with increase of sp³ fraction.

4. CONCLUSIONS

The effects of different substrate temperatures on the structural properties of pulsed laser deposited a-CN_x films are determined through Raman scattering analysis. The spectra were deconvoluted into Raman D and G peaks and the structural parameters are determined. The broad

spectra along with the Raman G peak position at 1532 and 1550 cm⁻¹ (downshift from single crystal graphitic peak at 1580 cm⁻¹) of Sample A and a-CN_x films, respectively, reveals amorphous nature of the film and have both sp² trihedral and sp³ tetrahedral bonds in its structure. Raman scattering studies observed that, Sample A and a-CN_x films deposited at RT to be amorphous in nature. The upward shifts of Raman G peak towards 1592 cm⁻¹ shows the evidence of a progressive formation of crystallites in a-CN_x films upon increase of ST. While, the upward shifts of Raman D peak towards 1397 cm⁻¹ have been related to the decreased of bond-angle disorder and sp³ tetrahedral bonding in its structure.

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