



A comparison study between atomic and ionic nitrogen doped carbon films prepared by ion beam assisted cathode arc deposition at various pulse frequencies



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ABSTRACT

A comparison study of microstructure and bonds composition of carbon nitride (CN_x) films fabricated at atomic and ionic nitrogen source by pulse cathode arc method was presented. The relative fractions of CN/CC bonds, N–sp³C/N–sp²C and graphite-like/pyridine-like N bonding configurations in the CN films were evaluated by combining C1s and N1s X-ray photoelectron spectroscopy with the hardness and optical band gap measurement. The dependence of microstructure (quantity, size and disordering degree of Csp² clusters) of CN_x films on the nitrogen source and pulse frequency was determined by Raman spectroscopy. Films with high atomic ratio of nitrogen/carbon (0.17) and high hardness were produced at ionic nitrogen source and low pulse frequency. The results showed that ionic nitrogen source facilitated the formation of CN bonds and N–sp²C bonding configurations (mainly in graphite-like N form). Moreover presenting an optimum pulse frequency (~10 Hz) led to the most nitrogen coordinated with sp³-C and the highest ratio of CN/CC bonds in the CN_x films. An equilibrium action mechanism might exist between the quantity and energy of carbon and nitrogen ions/atoms, giving more nitrogen-incorporated carbon materials. These allow us to obtain the high content of N–Csp³ bonding and expected bonding structure by optimizing pulse frequency and nitrogen source.

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1. Introduction

Carbon nitride (CN_x) thin films have recently attracted much interest since the theoretical prediction that a metastable phase of carbon nitride (β-C₃N₄) would be harder than or equal to diamond [1]. These films demonstrate superior properties than the respective carbon films in optical, electrical and mechanical applications [2–4]. The key to success in these properties of CN_x is the possibility for controlling the manner of nitrogen bonded with carbon and their relative content in the films. Although the experimental search of the crystalline C₃N₄ remains unsuccessful, the attempts to fabricate various dominative microstructures have also supplied potential ability for exploring both the expected structure and properties of the films, such as graphite-like, fullerene-like and pyridine-like structures arranged in layered, curved or cross-linking form [5–7]. These different configurations give the CN_x films

significantly difference in the electrical, optical and mechanical properties. Accordingly nitrogen substitution in carbon network plays an important role in the formation of such these structures, despite it bonded with sp³-coordinated carbon or with sp²-coordinated carbon.

Up to now, most of research works have been focused on the improvement of nitrogen content in the CN_x films by various deposition techniques and doping ways of nitrogen source [8–11]. Majumdar et al. [4,8] have prepared the hydrogenated carbon nitride films by dielectric barrier discharge plasma technique, and the average nitrogen content (N/C ≈ 0.76) in the films has been observed by changing the nitrogen partial pressure. Baptista et al. [9] have reported the formation of sp²-bonded hard amorphous carbon network in 400 keV N⁺-irradiated amorphous carbon and fullerene-like films. Cheng et al. [10] have studied that the nitrogen content in the carbon nitrogen films, deposited by direct current plasma assisted pulsed laser ablation, is greatly improved by using of direct-current glow discharge, and the fraction of the N–sp³C bonds increased with increasing the discharge voltage. Rodil et al. [11] have also found that Csp³ bonding to the highest N contents present in the carbon nitrogen films deposited using a low pressure, dual ion beam system, consisting of a filtered cathodic vacuum arc

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and a plasma beam source for carbon and nitrogen ions, respectively. Among of them, however, no studies on the interaction of varying quantity and energy of carbon atoms/ions with different nitrogen source have been reported. During pulse cathode arc deposition, the instantaneous quantity and energy of carbon plasma can be regulated by pulse frequency. Therefore carrying out comparison between atomic and ionic nitrogen doped CN_x systems prepared at various pulse frequencies can be useful for adjusting the microstructure, nitrogen composition and physical properties of CN_x films.

In this work, we fabricated CN_x films by introducing atomic and ionic nitrogen in the amorphous carbon network using ion beam assisted pulse cathode arc technique. Different pulse frequencies were used to achieve various quantities and energies of carbon ions/atoms during the films deposition. The effect of pulse frequency on the microstructure (the size and ordering of Csp^2 clusters) and bonding configuration of carbon and nitrogen atoms in the CN_x films was investigated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). XPS measurement provides insight into the chemical environment of nitrogen and carbon atoms in the CN_x films. Two and three main bonding states have been resolved for the N1s and C1s core-level spectra (detail interpretation seen in N1s section below), respectively.

2. Experimental

CN_x (N_2) and CN_x (N^+) films were synthesized on silicon (1 0 0) substrate using a typical cathode arc deposition device, as shown in reference [12]. A graphite target of 99.5% purity was used as pulsed evaporation cathode. Pulse frequency and pulse number were 3–20 Hz and 3000, respectively. The energy of the incident carbon atoms/ions onto the substrate can be varied by adjusting the pulse frequency. High purity N_2 (99.99%) was used as reactive gas to deposit CN_x films. CN_x (N_2) films were prepared at the nitrogen partial pressure of 0.04 Pa. CN_x (N^+) films were performed by introducing ionic nitrogen in the deposition process of carbon films. The N^+ ions were produced by ion sputtering source at the nitrogen partial pressure of 0.04 Pa. The energy of nitrogen ion beam was about 120–150 eV. Silicon substrate was ultrasonically cleaned in acetone, ethanol and deionized water for 20 min to remove other surface contaminants. At a base pressure of 6×10^{-4} Pa, the substrate was etched by Ar ion sputtering source for 15 min to clean the oxide layer on the surface. Ar^+ discharge current and voltage were about 3 A and 350 V respectively. The thickness of as-deposited CN_x films varied in the range of 175–200 nm, which were measured by a step device (Ambios Technology XP-2).

The microstructure of the CN_x films was analyzed using a Renishaw inVia Raman spectrometer. Raman spectra were excited with the 514.5 nm emitting lines from an Ar-ion laser at an incident power of 20 mW. The chemical composition and bonding states of the carbon and nitrogen atoms on the surface of CN_x films were characterized using a PERKIN-ELMER CHI5300 X-ray photoelectron spectroscopy (XPS) with Al $K\alpha$ radiation line (1486.6 eV) and a power of 250 W. The binding energy in the XPS spectra is calibrated by using C1s (284.6 eV). XPS C1s and N1s core level spectra are fitted using XPSPEAK software. The backgrounds were modeled by means of a Shirley function. The hardness of CN_x films was measured by AFFRI DM-8 Knoop sclerometer, and setting a rhombic pyramid diamond indenter with an angle of $172^\circ 30'$ between the long edge of rhombic pyramid. The indentation load and duration time were 490.3 mN and 10 s, respectively. Optical transmittance in the range of 200–1100 nm was carried out using a UV-visible spectrophotometer Cary-50 (Varian).

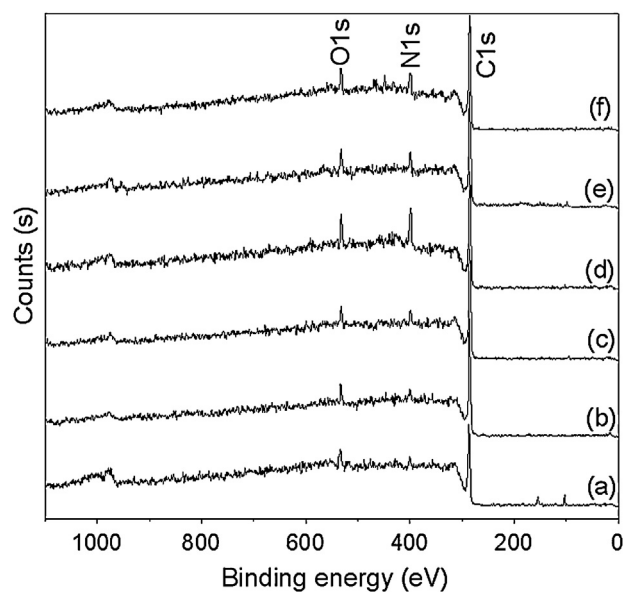


Fig. 1. Wide range XPS spectra of CN_x (N_2) and CN_x (N^+) films prepared at various pulse frequencies. Nitrogen pressure is 0.04 Pa; (a) CN_x (N_2 , 3 Hz); (b) CN_x (N_2 , 10 Hz); (c) CN_x (N_2 , 20 Hz); (d) CN_x (N^+ , 3 Hz); (e) CN_x (N^+ , 10 Hz); (f) CN_x (N^+ , 20 Hz).

3. Results and discussions

3.1. Chemical composition of CN_x films

XPS was used to investigate the chemical bonding of CN_x films. Fig. 1 shows XPS spectra of CN_x films prepared at various pulse frequencies by introducing N_2 and N^+ ions. Strong C1s, N1s, O 1s peaks, and weak Si 2s and Si 2p peaks can be observed in the spectra. The main sources of silicon and oxygen are the Si substrate and atmosphere. The atomic ratio of N/C on the surface of CN_x films is determined from atomic sensitivity factors method [13]: $\frac{n_N}{n_C} = \frac{I_N/S_N}{I_C/S_C}$, where n_N/n_C is the relative content of the N atom to C atom, I_N/I_C is the intensity ratio of the XPS peak of N and C atoms, generally corresponding to the ratio of whole integrated areas of the N1s to C1s peaks, S_N/S_C is the relative sensitivity factors of N and C atoms, here, $S_N = 0.48$, $S_C = 0.28$. The atomic ratios of N/C for CN_x (N_2) and CN_x (N^+) films prepared at various frequencies are summarized in Table 1.

The n_N/n_C on the surface of CN_x (N_2) films increases with increasing the frequency while that of the CN_x (N^+) films decreases with the frequency. It can be interpreted from the fact that at high pulse frequency evaporated carbon atoms/ions possess high instantaneous density and low energy on the substrate surface. In this case, low energy nitrogen atoms surrounded by carbon atoms/ions are difficult to diffuse and release from the CN_x (N_2) films, thus leading to the increase of nitrogen content with the frequency. However for high energy N^+ ions, which have enough mobility and reactivity in the carbon matrix, the high pulse frequency enhances the impact and reaction of nitrogen with carbon. This will lead the most of nitrogen atoms bonding with carbon and a few of isolated nitrogen presenting in the films due to the release of nitrogen in the form of gas. Moreover the nitrogen content in the CN_x (N^+) films is significantly higher than for the CN_x (N_2) films. This indicates that high energy nitrogen source facilitates the incorporation of nitrogen atoms with carbon due to the injection effect of high energetic N^+ ions.

Fig. 2 shows C1s XPS spectra of CN_x films prepared at various frequencies. The deconvolution of the peaks was executed by curve fitting using Gaussian–Lorentz function, which the Gaussian fraction retains with 20% for all films. The C1s region consists of two

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