Effect of Annealing on the Composition, Structure and Mechanical Properties of Carbon Nitride Films Deposited by Middle-Frequency Magnetron Sputtering

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Abstract

Carbon nitride films were deposited by middle-frequency reactive magnetron sputtering and annealed at different temperatures in nitrogen ambient. X-ray photoelectron spectroscopy, Raman scattering, transmission electron microscopy, and nano-indenter were used to characterize the as-deposited and annealed films. The analysis showed that annealing resulted in the dissociation of N and C in the films. The dissociation of C happened after 500 °C and lagged behind that of N. With the increase of annealing temperature, the disorder of sp2 C decreased and the films were gradually graphitized. The microstructure changed from amorphous to fullerene-like CNx with the annealing temperature increasing to 500 °C, and then to nitridized graphite nanocrystals at 600 °C. The graphitization resulted in a drastic decreasing of hardness and modulus of the films.

Keywords

Carbon nitride, Thermal properties, Nanocrystal, Microstructure, Hardness.

1. Introduction

Stimulated by the theoretical work of Liu and Cohen [1], [2], carbon nitride (CN_x) films have attracted much attention in the world and various techniques have been utilized to deposit this material [3], [4], [5], [6]. Although the existence of β-C_3N_4 phases is still debated, substiochiometric CN_x films have exhibited interesting properties such as extreme hardness, infrared transparency, chemical inertness, and excellent tribological, corrosion and biomedical properties [7].

At the course of application and post-treatment, the composition and structure of the carbon nitride films would inevitably be influenced by the ambient temperature. This would lead to the changes of the properties of the coatings. Therefore, it is necessary to study the thermal stability. Such kinds of studies are still limited and some of the results are even contradictory [8], [9], [10]. This work aims to elucidate, for the first time to our knowledge, the effect of annealing temperature on the microstructure and mechanical properties of sputtered carbon nitride films prepared by the newly developed middle-frequency magnetron sputtering technology on an industrial-scale machine [11].

2. Experimental detail

Carbon nitride films with a thickness of about 200 nm were deposited on Si (111) and cemented carbide substrates by middle-frequency reactive magnetron sputter of graphite target in a mixed N–Ar discharge. Deposition was performed with the total pressure kept constant at 4.0 Pa and at a N_2 fraction of 0.5. The substrate bias was fixed at 100 V, the temperature of the chamber was kept at 200 °C, and the distance between the target and substrate was 8 cm. The as-deposited films were then annealed at temperatures between 300 and 700 °C for 10 min in nitrogen ambient.

A combination of X-ray photoelectron spectroscopy (XPS), Raman scattering, and transmission electron microscopy (TEM) were used for the microstructure and chemical bonding investigation of the films. XPS measurements were performed using Mg K_α (1253. 6 eV) X-ray radiation in a Kratos2AXIS2HS XPS system. Before XPS measurements, Ar-ion etching of 10 min was carried out for every sample to eliminate the surface contamination. The Raman spectra were measured with a RM-1000 confocal Raman microspectrometer using an Ar-ion laser with an excitation wavelength of

514.5 nm. TEM was investigated by using JEM-2010FEF (UHR) TEM operated at 200 kV. The TEM specimens were obtained by the standard procedures of precision grinding, dimple grinding, and ion milling till perforation. The hardness and modulus was measured using MTS Nano-indenter XP.

3. Results and discussion

The N/C atomic ratios of CN_x samples were calculated according to the XPS peak areas of N and C and their sensitivity factors. Fig. 1 shows the dependence of nitrogen content on the annealing temperature. The as-deposited film exhibits the highest N content with an N/C ratio of 17%. With the annealing temperature being increased, the N content decreases and reaches a minimum N/C of 8% at 400°C. The decrease of N/C ratio is due to the dissociation of nitrogen. Deng and Souda [12] have determined the main desorbed species to be N_2 and C_2N_2 by using quadrupole mass spectroscopy. After 400°C the N/C ratio increases again. This is contrary to the result of vacuum annealing carbon nitride films [13]. We believe that the dissociates of C grow considerately at elevated temperature, C atoms of the films react with N_2 and residual O_2 in the annealing ambient, producing C_2N_2 and CO_2, and result in the increasing of N/C ratio. When annealing temperature increased to 700°C the film was entirely decomposed and the substrate was exposed.

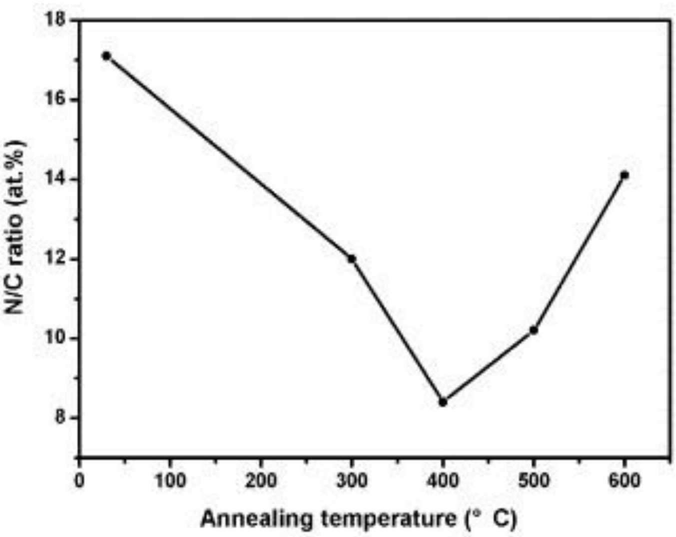

Fig. 1. N/C atomic ratio of the CNx films annealed at various temperatures.

Fig. 2 shows the Raman spectra of the CN_x films annealed at various annealing temperatures. The Raman active peaks of the films are observed at 700 (L peak), 1380 (D peak), 1550 (G peak), 2020, 2220, 2330, and 2900 cm^{-1}. The peak at 2020 cm^{-1} is due to the existence of sp^1 C. The peak at 2220 cm^{-1} characterizes the triply bonded carbon–nitrogen stretching mode. The very small peak at 2330 cm^{-1} coincides with the CO_2 stretch [14]. The G mode is the stretching vibration of any pair of sp^2 sites, whether in C-C chains or in aromatic rings. The D mode is the breathing mode of those sp^2 sites only in rings. According to Gaussian fitting results of D and G peaks (Table 1), with increasing the annealing temperature, D and G peaks shift up, the widths become narrow, and the I_D/I_G ratio increases. The up-shift of the peak position indicates the shortening of atomic distance of sp^2 C and enhancement of the bonding strength. The narrowing of the peak widths means the reduction of the disorder of the films. The increase of the I_D/I_G ratios corresponds to the transformation of the bonding configuration from the sp^2 C chains to aromatic rings. This trend is also consistent with the microstructure transformation from a-C to nc-graphite as illustrated by Robertson [15] and confirmed by TEM analysis (Fig. 3). Therefore, with the increase of the annealing temperature, the CN_x films are gradually graphitized. Another feature observed from Raman spectra is the weakening of sp^1 C peak with increasing annealing temperature, which reveals poorer thermal stability of sp^1 C compared with sp^2 C.

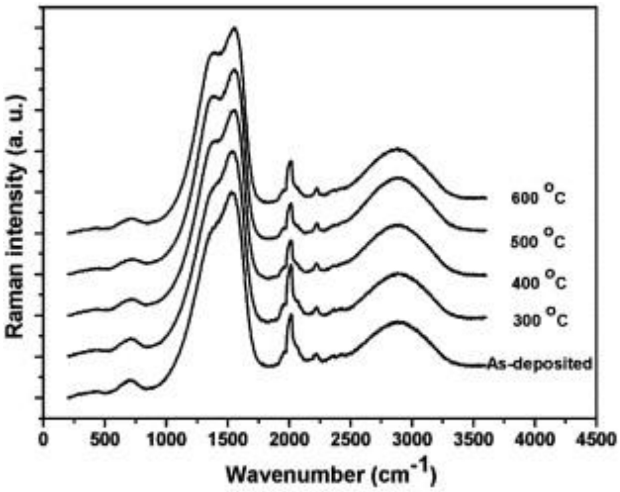

Fig. 2. Raman spectra of CNx films annealed at various temperatures.

Table 1 Wavenumber, full width at half maximum, and intensity ratio of D and G peaks obtained from fitting of Raman spectra with Gaussian functions of CNx films annealed at various temperatures

Annealing temperature (°C)	D peak position (cm−1)	D peak width (cm−1)	G peak position (cm−1)	G peak width (cm−1)	ID/IG
As-deposited	1370	363	1558	161	3.0
300	1376	360	1561	159	3.0
400	1382	359	1568	142	3.6
500	1383	349	1573	135	3.7
600	1384	348	1574	137	3.7

Fig. 3 shows the high-resolution TEM plan-view micrographs of the as-deposited and annealed CN_x films. The as-deposited film is totally amorphous (Fig. 3a). The samples annealed at 300 and 400 °C exhibited a similar structure. However, when the annealing temperature is increased to 500 °C, the film transforms to a fullerene-like microstructure (Fig. 3b). The fullerene-like sheets form well-aligned, multilayered spherical features, or the so called nano-onions [16], with successive shells with a spacing of about 0.33 nm. The micrograph was taken at a tear edge of a floated-off film, which shows a crack propagating along the outer shells of the individual features, indicating their substantial internal cohesive strength. Hellgren et al. [5] proposed a ‘‘defected-graphite’’ model to explain this transition from graphite-like to fullerene-like phase. They think that the incorporation of N promotes the formation of pentagons in the otherwise hexagonal graphite-like planes, and thus induces buckling of the basal planes which facilitates cross-linking between the planes through sp^3-coordinated C. After annealing at 600 °C, the sample exhibits an amorphous microstructure containing crystalline clusters about 3 nm in diameter (Fig. 3c). The spaceing of the crystallines is 2.79 nm corresponding with the (200) diffraction of N-graphite.

Fig. 4 shows the hardness and Young's modulus of the films as functions of annealing temperature. The as-deposited film exhibits a hardness of 13.8 GPa and a Young's modulus of 137 GPa. When the temperature is higher than 300 °C, the hardness and modulus begin to decrease drastically. Xu et al. [13] point out that the graphite plane structure curves and forms a fullerene-like structure, which may result in a sharp increase in stress and hardness of the CN_x films. At 500 °C where the fullerene-like structure is formed, the hardness and modulus is increased but is still lower than that of the as-deposited film. This is because in the whole annealing temperature range there is a graphitization process that weakens the mechanical properties. After annealing at 600 C, the film exhibits a hardness of 7.9 GPa and a Young's modulus of 95 GPa, consistent with the microstructure of nanocrystal graphites.

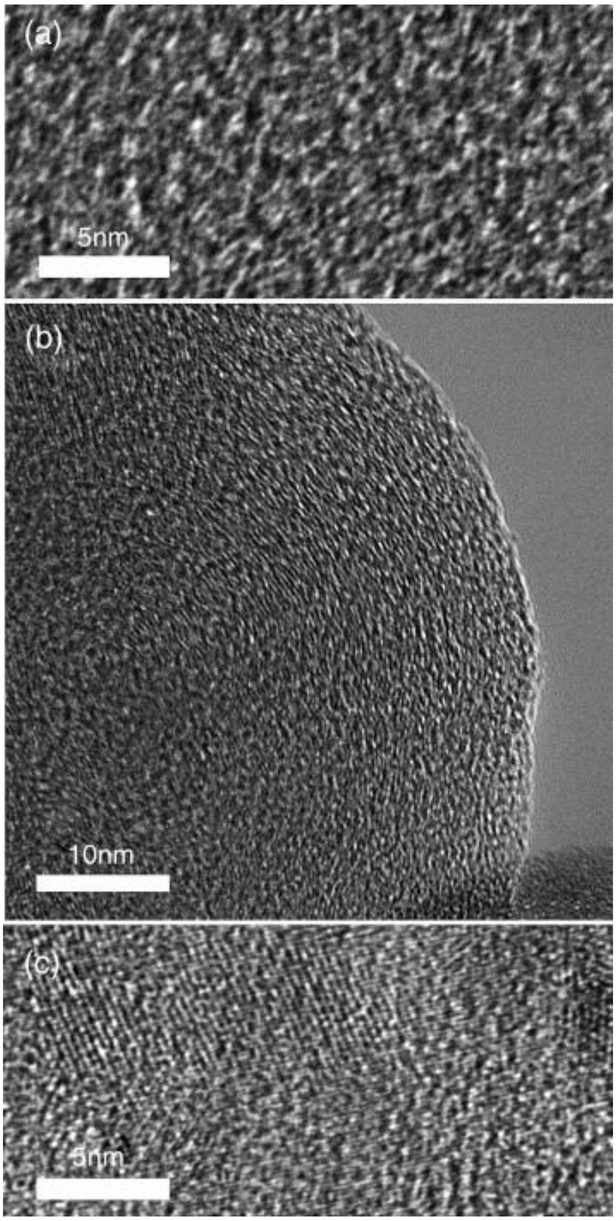

Fig. 3. High-resolution TEM images of CNx films: (a) as-deposited, (b) annealed at 500 °C and (c) annealed at 600 °C.

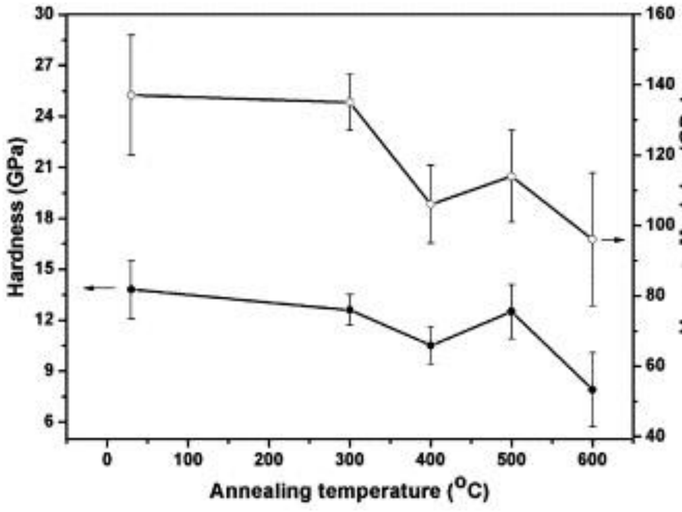

Fig. 4. Hardness and Young's modulus of CNx films annealed at various temperatures.

4. Conclusions

In summary, carbon nitride films were deposited by middle-frequency magnetron sputtering in N–Ar discharge. The films were annealed at different temperatures from 300 to 700 °C. The annealing resulted in the decomposition of the films, through dissociation of N and of C when the temperatures exceed 500 °C. With varying composition and annealing temperature, the microstructure of the films changes from amorphous to fullerene-like and graphitic crystallization. At elevated annealing temperature, the graphitization resulted in a drastic weakening of the mechanical properties of CN_x films.

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