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Bonding structure of a-CN_x:H films obtained in methane–nitrogen system and its influence on hardness

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Abstract

Hydrogenated amorphous carbon nitride (a-CN_x:H) films were deposited on silicon substrates by plasma enhanced chemical vapor deposition using methane and nitrogen mixture as precursors. The structure and mechanical properties of the as-deposited films were investigated by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and nanoindentation. Based on XPS and FTIR measurements, the nitrogen content in the films is revealed to about 28 at.% with a N/C ratio of 0.39 and N atoms are bonded to C atoms via forming C–N, C═N and C≡N bonds. In addition, the $-CH_x$ and $-NH_x$ groups in the films are detected by FTIR spectra. It is found that film hardness depends significantly on the ratio of the C–N to C≡N bonds and gradually increases with increasing N_2 fraction in the precursors.
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1. Introduction

Numerous attempts to synthesize carbon nitride films have been stimulated by the prediction proposed by Liu and Cohen that a new superhard phase β-C_3N_4 would have bulk modulus and hardness higher than those of diamond [1,2]. Since 1989, various synthesis methods have been adopted to grow CN_x films, including magnetron sputtering [3], ion implantation [4], plasma enhanced chemical vapor deposition (PECVD) [5,6], laser ablation [7,8] and ion beam deposition [9].

Among these methods, the PECVD technique enables a good film adhesion even if the substrate temperature is low. The PECVD using hollow cathode glow discharge (HCGD) is one of the promising techniques since a very effective ionization of the gas and vapor particles can be achieved [10]. In addition, the HCGD can be easily driven by direct current excitation and require no complicated source design [11].

There are many publications devoted to the identification of the origin of the subpeaks in both the C1s and N1s X-ray photoelectron spectroscopy (XPS) spectra. The most complete one is probably Ronning's review work [12], which contains an excellent review of other previous work as well. Ronning's interpretation may be correct, however, in our studies, there are large amounts of $-CH_x$ and $-NH_x$ groups as well as nitrile bonds in the as-deposited films, based on Fourier transform infrared spectroscopy (FTIR) spectra of the films. Therefore, Ronning's conclusion may not be proper for our work.

As for FTIR analysis, if carbon is sp^3 bonded to nitrogen as in crystalline β-C_3N_4, an absorption peak should appear around 1250 cm^{-1} as predicted by Wixom [13]. The observed C–N stretching frequency for molecules containing fairly symmetric tetrahedral carbon–nitrogen bonds (e.g., trimethylamine and hexamethlenetetramine) is in the 1050–1200 cm^{-1} range [13].

In this paper, we present a study of hydrogenated carbon nitride films deposited on silicon substrates by the PECVD with

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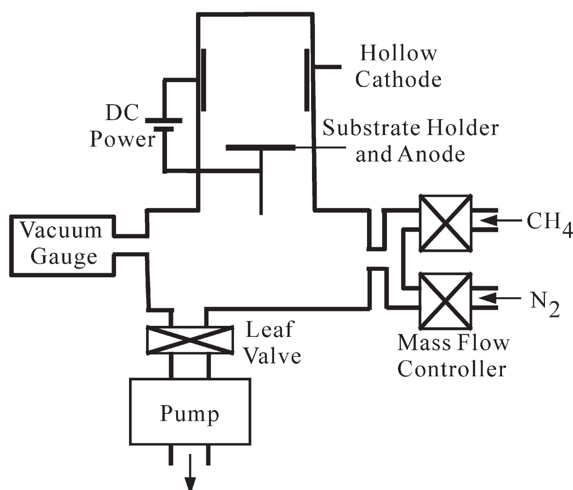

Fig. 1. The schematic diagram of the deposition apparatus.

methane and nitrogen mixture as precursors. The plasma was excited by the HCGD. XPS and FTIR analyses indicate that N atoms in the films are bonded to C atoms via forming C–N, C═N and C≡N bonds. The C–N/C≡N ratio deduced from the deconvolution of both C1s and N1s XPS spectra, is in good agreement with each other. The hardness of films increases gradually with increasing N_2 fraction in the precursors. Furthermore, the hardness depends largely on the ratio of C–N to C≡N bond. It is found that the amount of network terminating groups, i.e. C≡N, $-NH_x$ and $–CH_x$, reduces the film hardness.

2. Experimental details

The schematic diagram of the deposition system is shown in Fig. 1. The substrate holder was fixed on an axially movable anode, which was kept at the position with the high-density plasma to obtain a relatively higher concentration of dissociate atomic and ionized nitrogen species.

As shown in Fig. 1, the reactive gases were regulated downstream in the vacuum chamber, using mass flow controllers, 50 sccm full scale for nitrogen (99.999% purity) and 5 sccm full scale for methane (99.999% purity), respectively. During the deposition, the gas flow rate of CH_4 kept constant at 1 sccm, while the N_2 flow rate varied from 3 to 10 sccm. The other parameters were kept the same for all the films, the cathode-substrate distance was 2 cm and the deposition pressure was controlled at 1.0×10^2 Pa by a leaf valve.

A −350 V continuous voltage was applied, resulting in a relatively higher nitrogen content in the films and an acceptable deposition rate. In our early studies, we found that the nitrogen content in the films decreased with increasing voltage. A possible explanation to such a behavior is that the highly energetic species can break unstable CN bonds and create new CC bonds leading to a decrease of N atom incorporated in the films [14].

Prior to deposition, the silicon substrates were cleaned consecutively using ultrasonic in the acetone, absolute alcohol bath, then etched by the HF acid for 1 min to remove the oxide and finally rinsed with distilled water.

All the films were grown with a thickness of about 1 μm, measured by an α-step surface profilometer. The XPS data were obtained using an ESCALAB-250 spectrometer with a monochromatic Al K_α ($h\nu$ = 1486.6 eV, energy resolution of 0.6 eV) X-ray source. No sputtering etching was performed before XPS measurement. The analyzer is in the constant resolution mode, at pass energy of 20 eV. The XPS spectra were collected with take off angle of 90°. During XPS measurement, surface charge was compensated by using a flood gun. The FTIR absorption was measured using MAGNA750 over a wavenumber ranging from 400 to 4000 cm^{-1}. Nanoindentation tests were carried out to evaluate the mechanical properties of the film under a Nano Indenter XP instrument using an Accutip 4-1 tip. In order to obtain reliable values, measurements were performed with a maximum load of 20 mN, average values were calculated from five indentations on different sites of each specimen. During the test, the other main parameter used is as follows, surface approach velocity was 10 $nm\cdot s^{-1}$, surface approach sensitivity was 40%, and allowable drift rate was 0.05 $nm\cdot s^{-1}$.

3. Results and discussion

3.1. Element analysis

Based on XPS measurements, films with N content of 23–28 at.% have been grown if the contribution of oxygen was removed. The N/C ratio reaches up to 0.39 in the film with nitrogen content of 28 at.%. Table 1 shows the result of XPS for the films. Though the N_2/CH_4 flow ratio varies from 3 to 10, there is no distinct change of the N content in the film. The N/C ratio in the films does not vary extensively as well, just from 0.30 to 0.35, except the sample grown with the N_2/CH_4 flow ratio of 8. The N concentration seems to be saturated without reference to the N_2 fraction in the precursors. This behavior is also observed by Neidhardt [15] during the studies of Fullerrene-like (FL) CN_x films. Their studies indicated that most of the N incorporated in the films originated from already preformed C-containing species (C_xN_y, $x,y\leq2$) arriving at the substrate, which was a key factor for the evolution of FL–CN_x structure. However, plasma analysis reveals that the nitrogen content of the C-containing ions saturated regardless of the N_2 fraction in the discharge. This might correlate with the saturation of the film nitrogen content.

Table 1
Nitrogen concentration and N/C ratio of the films prepared using different N_2/CH_4 flow ratio

N_2/CH_4	N (at.%)	N/C
3	26	0.35
4	25	0.33
5	23.5	0.31
6	24	0.32
8	28	0.39
10	23	0.30

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