

Effects of nitrogen content on structure and electrical properties of nitrogen-doped fluorinated diamond-like carbon films

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Abstract: Nitrogen-doped fluorinated diamond-like carbon (FN-DLC) films were prepared on single crystal silicon substrate by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) under different deposited conditions with CF_4 , CH_4 and nitrogen as source gases. The influence of nitrogen content on the structure and electrical properties of the films was studied. The films were investigated in terms of surface morphology, microstructure, chemical composition and electrical properties. Atomic force microscopy (AFM) results revealed that the surface morphology of the films became smooth due to doping nitrogen. Fourier transform infrared absorption spectrometry (FTIR) results showed that amounts of $\text{C}=\text{N}$ and $\text{C}\equiv\text{N}$ bonds increased gradually with increasing nitrogen partial pressure r ($r=p(\text{N}_2)/p(\text{N}_2+\text{CF}_4+\text{CH}_4)$). Gaussian fit results of C 1s and N 1s in X-ray photoelectron spectra (XPS) showed that the incorporation of nitrogen presented mainly in the forms of $\beta\text{-C}_3\text{N}_4$ and $\alpha\text{-CN}_x$ ($x=1, 2, 3$) in the films. The current—voltage ($I-V$) measurement results showed that the electrical conductivity of the films increased with increasing nitrogen content.

Key words: fluorinated diamond-like carbon films; nitrogen doping; structure; electrical properties

1 Introduction

Fluorinated amorphous carbon (a-C:F) films are a kind of very interesting materials due to their outstanding properties, such as high hardness, low dielectric constant, low friction coefficient and wide optical band gap[1–5]. These films have been used in industry as dielectric interlayer in ultra-large scale integration technology devices, protective coatings on magnetic hard disks and optical devices coatings. The a-C:F films have excellent electrical and optical properties, good thermal stability and industrial process ability, due to C—F bonding and highly cross-linked structures of the films[6–8]. The thermal stability of the films depends strongly on the degree of cross linking in the carbon network, and the highly cross linking can be obtained by increasing the deposition power, deposition temperature, annealing temperature, and so on[1, 6, 9–10]. Ways to further

improve the properties of this material include incorporation of other elements and adjustment of the atomic content in the films[11–12]. LIU et al[10] found that the fraction of aromatic ring structures increases and the thermal stability of the films is strengthened with the increase of N_2 content. And nitrogen doping is a feasible approach to improve the thermal stability of films. YOKOMICHI and MASUDA[13] reported that a-C:F:N films had a low dimensional structure without crystalline regions, and the dangling bond density decreased and the optical band gap was approximately constant with increasing nitrogen concentration.

However, the structure and electrical properties are not very clear after the nitrogen doping of the a-C:F films. In this work, nitrogen-doped fluorinated diamond-like carbon (FN-DLC) films were deposited by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) using CF_4 , CH_4 and N_2 as source gases. The purpose of this work is to investigate

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the relationships between the local bonding configurations of the N atoms from the analysis of the Fourier transform infrared absorption spectrometry and X-ray photoelectron spectra in terms of C—N bonds vibration modes. The effects of nitrogen incorporation on the electrical properties of the films were mainly discussed.

2 Experimental

FN-DLC films were deposited on silicon (100) substrates by the radio frequency plasma enhanced chemical vapor deposition (RF-PECVD). The experimental equipment had been described previously in details[14]. The films were prepared under the following conditions: discharge power 100–120 W, and deposition temperature 80–100 °C. The source gases were CF₄, CH₄, and N₂. The CF₄ and CH₄ flow rates were fixed at 30 and 10 mL/min, respectively. The nitrogen partial pressure r ($r=p(\text{N}_2)/p(\text{CF}_4+\text{CH}_4+\text{N}_2)$) was varied from 0 to 0.33. That is to say, the N₂ gas flow was varied from 0 to 20 mL/min. Prior to deposition, the vacuum chamber was evacuated to 1.0×10^{-3} Pa. Before loading into the chamber, the substrates were cleaned in an ultrasonic bath of acetone and methanol for 10 min to remove residual organic contaminants, respectively, and then washed with deionized water and dried by blowing nitrogen gas.

In order to investigate the content of N and the electrical properties of the films, the surface morphology of the films was analyzed by NT-MDT type atomic force microscope (AFM). The chemical bonding configurations were characterized by a NEXUS 470 Fourier-transformed infrared spectrometer (FTIR). Information about the chemical bonding and the elemental composition of the films was obtained by X-ray photoelectron spectrometer (XPS). The effect of the doping nitrogen on the current—voltage (I — V) characteristics of the films was investigated by a micro-current instrument.

3 Results and discussion

3.1 Morphology of films

In order to investigate the effect of nitrogen doping on the surface morphology of FN-DLC films, the AFM images of the films grown with variation of nitrogen partial pressure of $r=0$, $r=0.20$ and $r=0.33$ are shown in Fig.1. The discharge power and temperature were fixed to be 100 W and 100 °C, respectively. The root mean square (RMS) surface roughness of the films deposited at a higher nitrogen partial pressure of $r=0.33$ is 6.173 nm, as shown in Fig.1(a), which is larger than that deposited

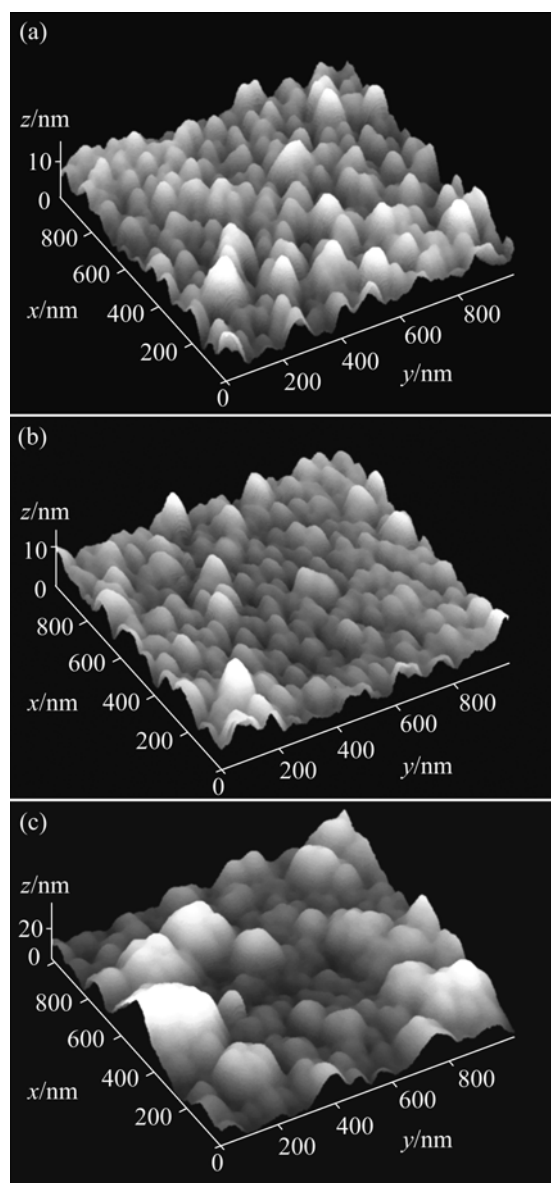


Fig.1 AFM images of films deposited at various nitrogen partial pressures: (a) $r=0.33$; (b) $r=0.20$; (c) $r=0$

at lower nitrogen partial pressure, as shown in Fig.1(b). When the nitrogen partial pressure is $r=0.20$, the RMS surface roughness is 5.035 nm. Whereas, The RMS surface roughness of the films deposited at nitrogen partial pressure of $r=0$ is 2.358 nm, as shown in Fig.1(c). It is surprising that the smoothest film is the one grown at the lowest nitrogen partial pressure of $r=0$. From the image of the surface as shown in Fig.1(a), it can be seen that the films have tightly packed configuration and smooth surface morphology. Those observations suggest that the films grown at lower nitrogen partial pressures by RF-PECVD were bombarded by energetic particles, which make the surface energy of the films decrease. That is to say, the surface morphology of the films becomes smooth due to doping nitrogen.

3.2 FTIR analysis of films

The changes in chemical bonds of the FN-DLC films with various nitrogen partial pressures are shown in Fig.2. The films were deposited at 120 W and 100 °C in a total pressure 6.2–7.0 Pa. It is obvious that the chemical bonding structures were strongly influenced by nitrogen partial pressure. As shown in Fig.2, the strong peak at around 1 100 cm⁻¹ corresponds to CF_x (x=1, 2, 3) groups vibrations, CF(1 030 cm⁻¹, 1 070 cm⁻¹), CF₂ (1 050 cm⁻¹, 1 160 cm⁻¹, 1 220 cm⁻¹) and CF₃ (980 cm⁻¹, 1 340 cm⁻¹)[6, 15]. The peak approximately at 1 600 cm⁻¹ corresponds to the unsaturated double bonds C=C and F₂C=C. The peak at 1 710 cm⁻¹ is associated to aromatic C=C stretching or F₂C=C stretching vibrations. The peaks at 1 634 cm⁻¹ and 1 694 cm⁻¹ can be attributed to the stretching of olefinic C=C and C=N[15–16]. Usually, C=N stretching frequency occurs in the range of 1 650–1680 cm⁻¹[6]. Also, it is observed that the absorbance corresponding to C≡N bond at 2 200 cm⁻¹ appears at the nitrogen partial pressure of *r*=0.20, while the absorbance for C≡N bond is not found when *r*=0. In a word, the results demonstrate that the nitrogen has been doped in the films, and nitrogen has combined with carbon atoms to form a chemical bond of C=N and C≡N.

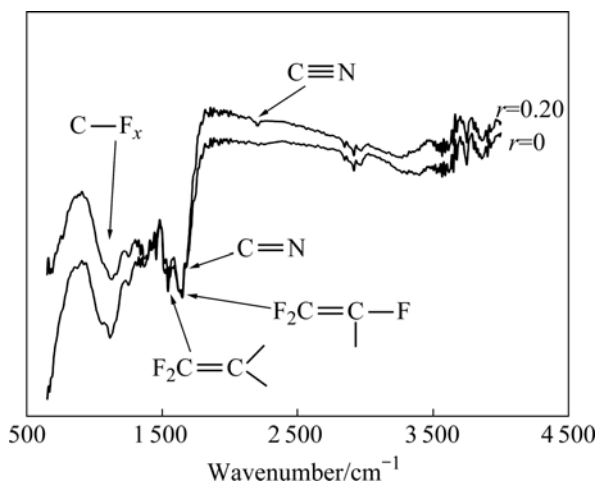


Fig.2 FTIR spectra of FN-DLC films deposited at various nitrogen partial pressures

In addition, the relative molar concentration of nitrogen, fluorine and carbon can also be estimated from the integrated absorbance of the band in the films. Here, the molar concentration was obtained by the Beer's law[17]:

$$n_i = A \int \frac{\alpha(\omega)}{\omega} d\omega \quad (1)$$

where n_x is the concentration of atom i ; A is the proportionality factor; and $\alpha(\omega)$ is the absorption coefficient at frequency ω . By Eq.(1), nitrogen, fluorine

and carbon molar concentrations of the films are calculated and then the nitrogen-to-carbon molar ratio of the films is obtained.

3.3 XPS analysis of films

Fig.3 shows a typical XPS spectrum of FN-DLC films deposited by RF-PECVD. The peaks at 286, 402, and 689 eV can be due to the photoelectrons exited from the C 1s, N 1s, and F 1s levels, respectively[18]. This indicates that the deposited films were mainly composed of carbon, nitrogen and fluorine atoms. Meanwhile, there is a peak at 535 eV in the XPS spectrum, which is due to photoelectrons exited from the O 1s. The O element in the films come from two tracks: 1) there is some H₂O remainder in the vacuum chamber before deposition, and it is involved in reaction when the films grow; 2) the sample surface of FN-DLC films is oxidized by O₂ before XPS test. Fitting the XPS spectra using Gaussian distribution, the abundance of the C—F and C—N bonding can be obtained. The following factors were considered in the curve-fitting process. The C 1s peak was assumed to consist of two peaks, the sp³ peak and sp² peak[18]. As seen in Fig.4(a), the two fitting peaks at 287 and 289 eV correspond to the sp² peak and sp³ peak, respectively. The N 1s peak was assumed to consist of two peaks, the N-sp³C peak and N-sp²C peak[19]. Fig.4(b) shows a typical fitted result of the FN-DLC films. According to the studies of WU et al[19] and MARTON et al[20], the peak at 398 eV was associated with the bond of N to sp³C of the β -C₃N₄; while the peak at 400 eV corresponds to the bond of α -CN_x (x=1, 2, 3). The peaks at 289 and 398 eV were taken as a pair and were assigned to C¹ and N¹ peaks of phase 1, which resembled those of the predicted β -C₃N₄ structure containing only C—N bonds. The peaks at 287 and 400 eV were taken as another pair and were assigned as C²

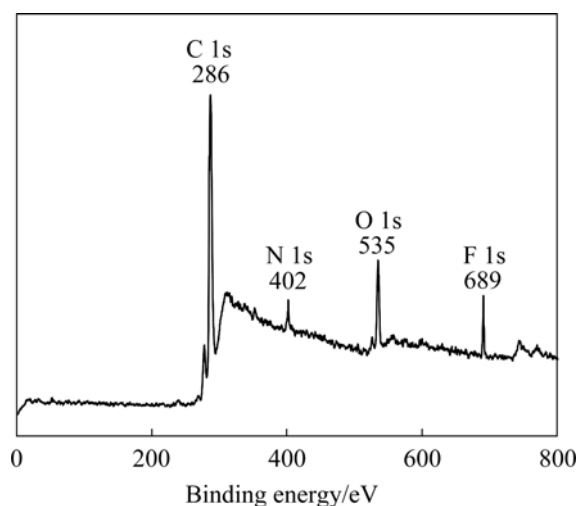


Fig.3 XPS spectrum of typical FN-DLC films

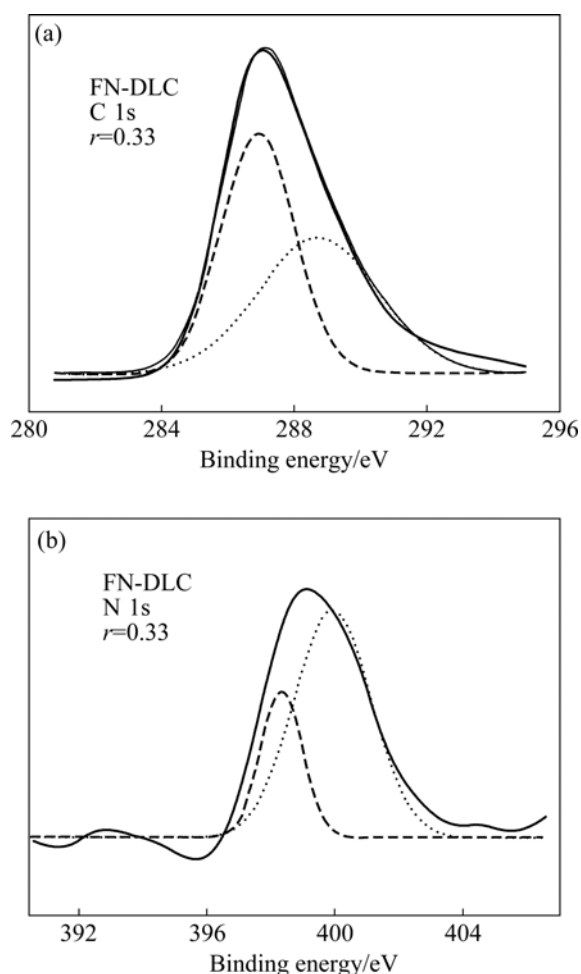


Fig.4 Fitted curves of typical FN-DLC films: (a) C 1s peak; (b) N 1s peak

and N^2 peaks of phase 2, which represented $a-CN_x$ phase[21].

3.4 Electrical conductivity of films

The current—voltage curves of FN-DLC films deposited at various nitrogen partial pressures are shown in Fig.5. It is obvious that the incorporation of nitrogen in the film changed the electrical conductivity. The electrical conductivity of the films increases with increasing nitrogen content. FTIR spectra results show that the nitrogen content in the films increases with the increase of nitrogen partial pressures. We think that the nitrogen in two kinds of films has different effects on the electrical conductivity. Because of the doping nitrogen in the films, a large amount of C and N atoms can form the $C-N_x$ bonds, and as an impurity center it has activated the films conductivity performance, which leads to the increase of the electrical conductivity. On the other hand, when the nitrogen partial pressure increases to a certain value, the nitrogen content in the films reaches saturated

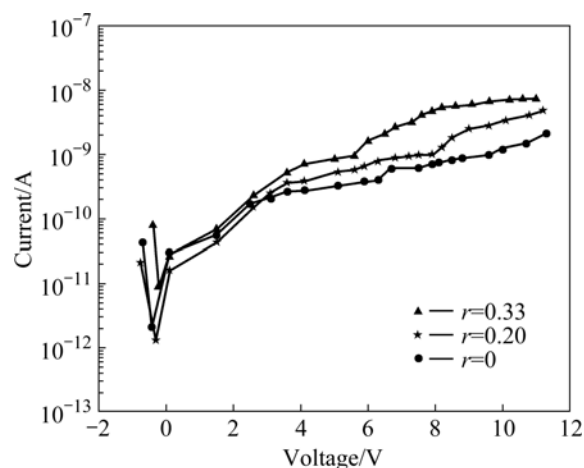


Fig.5 Current—voltage curves of FN-DLC films deposited at various nitrogen partial pressure

states, and there appear nonconductive phases, and the nitrogen atoms do not contribute to the electrical conductivity[21].

4 Conclusions

1) FN-DLC films were prepared by PECVD using CH_4 , CF_4 and N_2 as source gases, at various nitrogen partial pressures. The chemical bond of the films changed after the doping nitrogen, and the bond of $\beta-C_3N_4$ and $a-CN_x$ ($x=1, 2, 3$) appeared in the films.

2) The N atoms acted as activation atoms in the films, and the electrical conductivity of the films increased with increasing nitrogen content in the films. But, when the nitrogen content in the films reached saturated states, the electrical conductivity of the films remained unchanged.

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