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The study of surface energy, electrical properties and platelet adhesion behavior of a-C/a-CN films synthesized by PIII-D

F. Wen[1,2,a], N. Huang[2,b*], H. Sun[2], A. S. Zhao[2], J. Wang[2], Yu-Jie Li[3], Ze-Wen Wang[3]

[1] Key Laboratory of Tropical Biological Resources of Chinese Education Ministry, School of Science & Engineering, Hainan University, Haikou City 570228, P.R.China;

[2]Key Lab. of Advanced Technologies of Material Ministry of Education, School of Material science and Engineering, Southwest Jiaotong University, Chengdu city 610031, P.R.China;

[3] School of Material science and Engineering, Northwest Polytechnical University; State Key Lab. of Solidification Processing, Xi'an city 710072, P.R.China

[a]fwen323@163.com, [b]*nhuang@263.net

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Abstract: Amorphous carbon (a-C) and carbon nitrogen (a-CN) films were synthesized using plasma immersion ion implantation and deposition (PIII-D) under different N_2 flow at room temperature (R.T.). Lifshitz-van der Waals/acid-base approach (LW-AB) was introduced in order to study films' surface energy deeply. The results showed that the capability of the surface of the film on receive electron changed with N_2 flow, which effected platelet adhesion of film strongly. Hall effects tests were employed to characterize the electrical properties of the films. The results showed that the as-deposited films exhibited n-type semiconductor characteristic, and carrier concentration of the films decreased with N_2 flow increasing. Raman spectra with 514nm laser-source were employed to analyze the structural of the films.

Introduction

Since the suggestion of Liu and Cohen [1] of β-C_3N_4 as a new hypothetical superhard compound in 1989, great interesting were given by many researchers and a lot of efforts have been undertaken to synthesize this new superhard materials [2-5]. It was known to all that a-CN films have many excellent properties, such as high hardness, chemical inertness, smooth surface, low friction coefficient, superior wear resistance and deposition at room temperature(R.T.) [6], so a-CN films have been used in the fields of compute and hard disks widely [4].

In spite of much research work about CN film, but the researches have been mainly emphasized on mechanical properties, structure and composition, few research results on relation of electrical properties, surface electron structure and blood compatibility were reported. The work on electrical properties and blood compatibility is valuable. Furthermore, it is not reported that surface energy of a-CN films have been researched using Lifshitz-van der Waals/acid-base approach (LW-AB) [7] at present.

In this paper, the effect of process parameters to surface energy, electric properties and structure of a-C and a-CN were studied by many measurement and test methods.

Experimental and Methods

a-C and a-CN films were synthesized using PIII-D under different N_2 flow at R.T on Si(100) wafer. The N_2 flow changed from 0 to 10 sccm. A high purity (99.99%) graphite cathode was used to serve as the carbon plasma source. The parameters were listed in table 1. The samples were cleaned in turn by acetone, alcohol and deionized water. Vacuum system pressure was about 6.6×10^{-4} Pa. The samples were sputtering cleaned for 10 min using Ar^+ formed by 500W R.F. power and a 1 kV negative substrate bias voltage in order to eliminate the contamination on the sample surface.

Table 1 Parameters of synthesized N-doped DLC film by PIII-D

Sample No.	N0 (a-C)	N1	N2	N3	N4
N_2 flow (sccm)	0	1.2	3.0	6.0	10
Negative bias voltage & deposition time	i) Base Layer: Pulse 1.5KV+Direct current 50V (10 minutes) ii) Outer layer: Direct current 50V (10 minutes)				
Cathode Arc Source parameters	Magnetic current: ~10A, Average arc current: 8~9A The frequency of metal source: 60 Hz, Pulse Width: 1 ms				

Thickness of films was about 200 nm using Alpha-Step®-500 surface profile device. Contact angle measurements by the sessile drop technique using a contact angle geniometer (JY-82, China) were conducted at 25°C with doubly distilled water, formamide and diiodomethane as wetting agents. Lifshitz-vander Waals/acid-base approach (LW-AB) was introduced in order to study films' surface energy deeply. The Hall effects measurement was used to estimate the carrier current concentration and carrier current mobility rate of as-deposited films. The anticoagulant property of a-C and a-CN films was valuated from an aspect by platelet adhesion experiment in vitro. The structure of the films was measured by Raman spectra with 514 nm laser-source (T6400 type, Jobin Yvon Co., France).

Results

A series of contact angle data on a given surface yields the surface free energy components by fitting the data by LW-AB [8]. The Total surface energy (γ_s) can be expressed as Eq.1

$$\gamma_s=\gamma^{LW}+\gamma^{AB} \qquad (1)$$

Unlike γ^{LW}, the nonpolar London–van der Waals component, the acid–base component γ^{AB} comprises two non-additive parameters. These are the electron-acceptor surface tension parameter (γ^+) and the electron-donor surface tension parameter (γ^-), and the acid–base interactions are complementary in nature. The total acid–base contribution to the surface tension is given by Eq.2

$$\gamma^{AB}=(\gamma^+\gamma^-)^{1/2} \qquad (2)$$

We can infer the capacity of electron-accepting or electron-donor of films' surface based on the ratio of γ^+ to γ^-(γ^+/γ^-). The results of surface energy were shown in Fig.1. It can be seen from Fig.1 that γ^+/γ^- changed obviously among the different films. When N_2 flow (sample N3) is 6 sccm, the γ^+/γ^- take minimum value 0.32, which indicated the capacity of electron-accepting of sample N3 is the smallest.

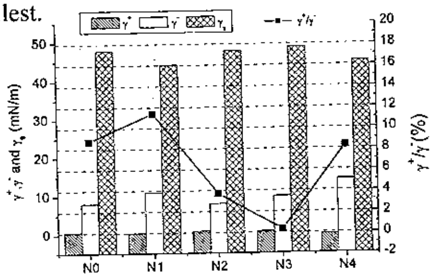

Fig.1 The graph of series surface energy parameters (γ_s, γ^+ and γ^-) as well as γ^+/γ^- of synthesized a-C and a-CN films (The process of N0~N4 seen in Table 1)

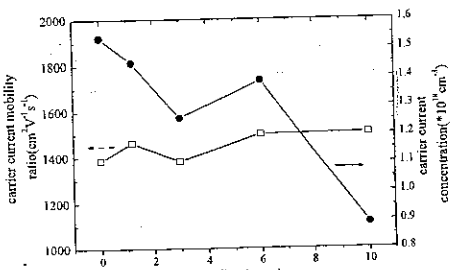

Fig.2 The curve of carrier current concentration and carrier current mobility ratio of a-C and a-CN films vs. N_2 flow

Hall effects tests were employed to characterize the electrical properties of the films. The results showed that the as-deposited films exhibit n-type semiconductor characteristic, and carrier current concentration of the films decreased with N_2 flow increasing (seen in Fig.2), but the carrier current mobility ratio rose little and kept same order of magnitude.

The anticoagulant property was evaluated utilizing the in vitro platelet adhesion test from one aspect. The samples (including Ti6Al4V, as compared sample) were incubated in a fresh human platelet-rich-plasma (PRP) at 37°C for 2 hours. After rinsing, fixing, and critical point drying, the specimens (morphology of adhered platelets) were examined using SEM (seen in Fig.3). It can be seen that transformation and accumulation of platelets of sample N3 was much less compared to DLC and Ti6Al4V, only few platelets germinated pseudopod and gather. The results showed that the actions (numbers and conformation) of adhesion platelet will be better with N_2 flow increase. But when N_2 flow continued increasing, the actions of adhesion platelet changed worse (seen in sample N4). For all of the films, sample N3 showed the best anticoagulant property.

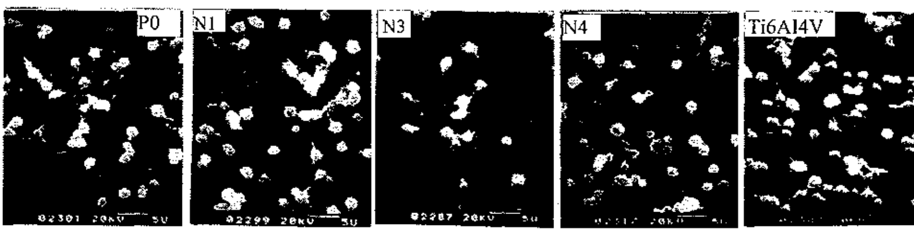

Fig.3 Morphology of adherent platelets on the as-deposited a-C and a-CN films (2 hours incubation in PRP at 37 °C)

Fig.4 showed the Raman spectra of as-deposited films on Si(100). From inspection of the spectra, it is interesting to note that the symmetric center shifted towards low frequency, which express that the threefold band disorder intensified [9] with N_2 flow increase.

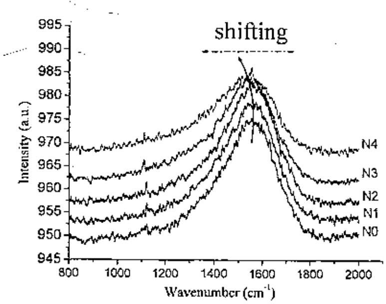

Fig.4 Raman spectra of as-deposited films (sample No. were marked in graph)

Discussion

Nitrogen doping made the surface electron structure change. The decrease of γ^+/γ showed that electron-donor surface tension parameter was superior to electron-acceptor surface tension parameter. Prof. Huang indicated that it should be effective to prohibit the absorption of "harmful" protein such as fibrinogen or globulin on to material surface and be favorable to absorb the "good" protein as albumin on the surface, and the artificial surface can prevent the absorbed protein from becoming denatured [10]. It has been proved that the denature of fibrinogen is related to the charges of fibrinogen transferring to the material and then the fibrinogen decomposed into fibrin monomer and fibrinpeptides [11]. So the surface of synthesized a-CN films can prevent fibrinogen to release and transfer electron to films' surface effectively. On the other hand, the n-type semiconductive a-CN films with high Fermi level can decrease the work function of the film, which makes electron move out from the film easily. Furthermore, compared to a-C films, the decrease of carrier current concentration of the a-CN films maybe lead to charge transfer difficultly. All of these causes make the a-CN film have super anticoagulant property.

Conclusions

The synthesized a-CN films have good anticoagulant property. Nitrogen doping can change surface electron structure of the films and affect blood contact properties of the films. When N_2 flow located suitable value, synthesized film can obtain super anticoagulant property. Furthermore, the surface energy study method of LW-AB, combining with Hall effects measurement result, is beneficial to explain the contact behavior of material with protein in blood and comprehend anticoagulant mechanism of material. But further research work need to be done in order to understand blood-contact behavior.

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