

## The Synthesis and Initial Studying Anticoagulant Property of O-Doped DLC Films By DC-MFCVAD

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**Keywords:** O-doped DLC, cathodic arc deposition, anticoagulant property, surface energy

**Abstract.** O-doped Diamond-Like carbon (O-DLC) films were prepared by direct magnetic filtered cathodic vacuum arc deposition (DC-MFCVAD) under different O<sub>2</sub> gas flow at room temperature (R.T.). Raman spectra were used to characterize structure of films. The wettabilities of the O-DLC films also were investigated by contact angle measurements using four common liquids. For studying films' interaction with blood, platelet adhesion experiment in vitro was done to characterize anticoagulant property of the O-DLC films from an aspect. Furthermore, ultraviolet spectrophotometer was employed to measure the optical band gap of the synthesized films. All of the results showed that O-DLC films have good anticoagulant property, oxygen doping can prevent graphite-like tendency of DLC films and increase band gap in a way, this kind of film materials may be become a new candidate biomaterials.

### Introduction

Diamond-Like carbon (DLC) films have many super properties, such as high conductivity, high wear-resistant, low friction coefficient, high hardness, chemical inertness etc [1-4], so DLC films were given great interesting for electronic and mechanical industry fields [2,3,5]. Furthermore, in the past twenty years, many researchers have studied and found DLC films possess good biocompatibilities, which makes DLC films also selected as biomaterials [6,7]. It was still dissatisfactory with blood compatibility of DLC films to be used in clinical anticoagulant biomedicine materials, despite the fact that many methods, such as doping and annealing etc. have been used to improve the blood compatibility of DLC films [8-12]. So, improving anticoagulant property of DLC films is a valuable work. It have been reported that blood compatibilities are related to composition, structure, wettability of films materials which can be adjusted by doping different element into DLC films[8-10,12].

Up to date, few people have studied oxygen-doped DLC film. In this paper, O-DLC films were prepared and studied initially. For studying the changes of properties when oxygen element was doped into DLC films, DLC films without doping any element also was synthesized.

### Experimental

O-DLC films were prepared on Si(100) wafers by DC-MFCAD at R.T. under different O<sub>2</sub> gas flow. The flow of O<sub>2</sub> changed from 5 to 30sccm. A high purity (99.99%) graphite cathode was used to serve as the carbon plasma source. The process parameters were listed in table 1. The samples were

cleaned in turn by acetone, alcohol and deionized water. Vacuum system pressure was about  $6.6 \times 10^{-4}$  Pa. The samples were sputtering cleaned for 10 min using Ar ions formed by 800 W ECR power, and a 1.6 kV negative substrate bias voltage. The structure of the films was measured by Raman spectroscopy (T6400 type, Jobin Yvon Co., France). The Si(100) wafers were only partially coated so that we could measure the film thickness using a step device (Alpha-Step®-500) surface profiler, the measured film thickness was about 400 nm. The wettability of the O-DLC films was investigated by contact angle measurements. The anticoagulant property of O-DLC films was valued from an aspect by platelet adhesion experiment in vitro. The transmittance of formed O-DLC films was measured by an ultraviolet-visible spectrophotometer.

Table 1 Synthesis parameters of the a-C:H films synthesized by PIH-D

Sample No.	D0	D1	D2	D3	D4
O <sub>2</sub> flow [sccm]	0	5	10	20	30

## Results and Discussion

Raman spectrum with 514 nm laser-source was used to characterize structure of the films. Raman spectra were fitted into two peaks (G-peak and D-peak) by Gauss method (seen in Fig.1). It can be seen from Fig.2 that  $I_d/I_g$  decreased and G-band FWHM (full width at half maximum) increased with O<sub>2</sub> flow increase. The Raman results showed that DLC films become less graphite-like with O<sub>2</sub> flow increase. But with continuing increasing O<sub>2</sub> flow, DLC films tended to more graphite-like again. At the same time, the intensity of the second-order Si peak at about  $960 \text{ cm}^{-1}$  enhanced, indicating that the films become more transparent when more O atoms are incorporated into the films [13].

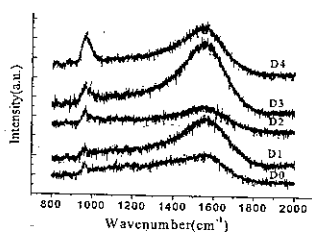


Fig.1 Raman spectra of the O-DLC films, Sample No. were marked in figure.

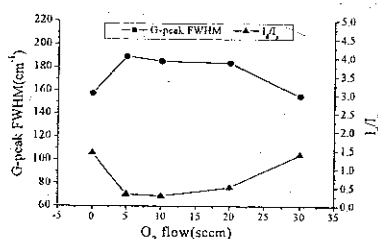


Fig.2 The curves of G-band FWHM and  $I_d/I_g$  vs. O<sub>2</sub> flow

The wettability of the O-DLC films was investigated by contact angle measurements using four common liquids. Detailed method was described in ref. [6]. The surface energy  $\gamma_s$  (including polar parts  $\gamma_s^p$  and dispersion parts  $\gamma_s^d$ ) can be obtained. For obtaining more information,  $\gamma_s^p/\gamma_s^d$  and  $\gamma_{sw}, \theta_w$  ( $\gamma_{sw}, \theta_w$ : interface tension and contact angle of the film and doubly distilled water) also were calculated. A phenomenon can be observed from Fig.3 that  $\gamma_s$  and  $\gamma_s^p/\gamma_s^d$  increased with O<sub>2</sub> flow, but  $\gamma_{sw}$  and  $\theta_w$  decreased. The surface energy results of the O-DLC films showed that films will become more hydrophilic with O<sub>2</sub> flow increase.

For studying films' interaction with blood, platelet adhesion experiment in vitro was done to characterize anticoagulant property of the O-DLC films from an aspect (Ti alloy was also selected as compared sample). The experiment method was described in ref. [6]. Adhesion platelet morphology was observed by SEM using amplified factor 1000 $\times$  and 3000 $\times$  respectively. The former, name as smaller amplified factor, was used to observe platelet quantities, and later was to platelet conformation. It can be seen from Fig.4 that transformation and accumulation of platelets of sample D2 was much less compared to DLC and Ti alloy, only few platelets germinated pseudopod,

majority platelets were unactivated and nearly round. The anticoagulant property of the films was improved slightly due to oxygen doping.

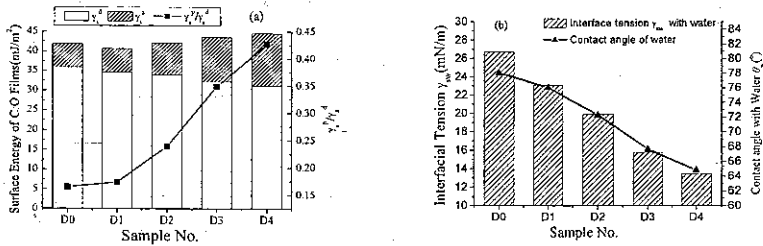


Fig.3 The results of surface energy of synthesized O-DLC films, (a)  $\gamma_s^d$ ,  $\gamma_s^p$  and  $\gamma_s^p/\gamma_s^d$ , (b)  $\gamma_{sw}$ ,  $\theta_w$

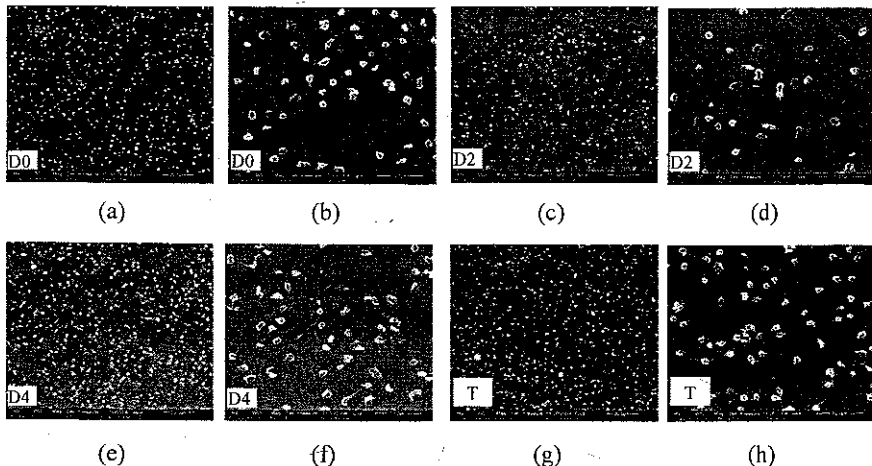


Fig.4 Morphology of adherent platelets (incubation time=2 hours) on DLC films: (a),(c),(e) and (g) were amplified 1000 times, (b),(d),(f) and (h) were amplified 3000 times.

Notes: i) Sample No. were marked lower left quarter of photo, ii) Mark T was Ti alloy samples

Optical band gap is a very important optical property. An ultraviolet spectrophotometer in the region 200~1100 nm was employed to measure the absorption coefficient  $\alpha$  of the synthesized DLC and part O-DLC films on glass. To estimate the optical band gap  $E_g$ , a Tauc's plot is constructed in which  $\alpha$  is plotted against the photon energy  $E$ .  $E_g$  can be deduced from the intercept of the extrapolated straight lines with the  $E$  axis. The method was described in ref [14]. The curves of absorption coefficient  $\alpha$  and band gap of synthesized DLC films were shown in Fig.5. The variation of  $\alpha$  and the deduced optical band gap of the O-doped films from Fig.5 showed that oxygen doping increased band gap of DLC in a way.

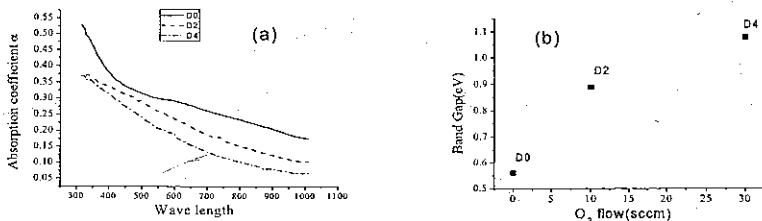


Fig.5 The plots of (a) absorption coefficient plot (sample No. were marked in figure) and (b) band gap vs.  $O_2$  flow

## Conclusions

It can be seen from above discussions, O-DLC films have good anticoagulant property when O<sub>2</sub> flow was fairly small. Oxygen doping can prevent graphite-like tendency of DLC films and increase band gap in a way. Some useful and interesting results were obtained by initial studying of O-DLC films. It should be significant work to continue researching O-DLC films, this kind of film materials may become a new candidate biomaterials.

## Acknowledgements

The work described in this paper was jointly supported by Chinese NSFC 30270392.

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