

Synthesis and characterization of high voltage electrodeposited phosphorus doped DLC films

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Received 13 December 2007; received in revised form 3 January 2008; accepted 7 January 2008

Available online 12 January 2008

Abstract

Phosphorus doped diamond like carbon (DLC) films were firstly synthesized by the electrolysis of methanol-Triphenylphosphorus (PPh₃) solution under high voltage, atmospheric pressure and low temperature. The microstructure and morphology of the as-deposited films were analyzed by Raman spectroscopy, X-ray photoelectron spectroscopy, and atomic force microscopy. The measurements results suggested that phosphorus doping enhanced the carbon films graphitization and the doped phosphorus existed mainly in C=P bonds with the P/C ratio of 0.034. The P-DLC films have larger surface roughness compared to the DLC film. Moreover, the formation of P-DLC films in liquid-phase electrodeposition was via the reactions of the –CH₃ and –P groups to form CP_x network.
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Keywords: DLC; Phosphorus carbide; Electrodeposition; Growth mechanism

1. Introduction

Widespread interests have been aroused in diamond like carbon (DLC) films as the cold cathode device and field emission displays due to their low surface work function, compatibility with existing in the microelectronic process technology [1,2]. Moreover, diamond like carbon films have similar properties of diamond, such as high hardness, high wear resistance, excellent chemical inertness, high thermal conductivity, etc. Phosphorus was widely used as n-type dopant in silicon [3]. When P was introduced, the resistivity of DLC films could decrease by 6–7 orders of magnitude even at the concentration of P in carbon films of only 1% [4]. Golzan et al. [5] reported that the phosphorus with a content of 3% in the carbon films could destabilize the tetrahedral network in favor of a sp² bonded network. Frederik Claeysens and his

coworkers [6] declared that phosphorus carbide could be formed in higher phosphorus content, similar to carbon nitride. The phosphorus incorporated into diamond like carbon film promoted electrons to emit from the conduction band, further enhanced the field emission threshold density and the optical band gap [7]. In addition, Sunny et al. [8] reported that platelet adhesion and activation are suppressed on the phosphorus doped diamond like carbon films, which exhibited excellent wettability, suggesting the good hemocompatibility of P-DLC film. So phosphorus doped DLC films displayed the potential applications in the electronics device and biomedical engineering, such as the microelectrode materials, the cold cathode materials and the medical implant with good biocompatibility, etc.

Various physical vapor deposition techniques have been used to prepare the phosphorus doped carbon films such as plasma immersion ion implantation and deposition [9], capacitively coupled radio frequency plasma deposition [10], filtered cathodic arc method [4], and pulsed laser

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deposition [11], etc. From the view of the practical applications, the liquid deposition technique had many advantages over PVD techniques, such as low deposition temperature, simplicity of experimental setup, and availability of coating on substrates with complex shapes, liquid-phase deposition became more attractive. The deposition of DLC films via electrolysis of organic liquid such as ethanol and methanol has been demonstrated recently, and many groups made great effort to investigate the electrochemical deposition process and the structure characterization by choosing different organic carbon source [12–14]. Lately, copper incorporated into diamond-like carbon film was prepared by the electrochemical method using the electrolyte of the copper salt solution reported by Jiang et al. [15] and Huang et al. [16]. Yan et al. [17] have reported that nitrogen-doped diamond-like carbon films could be obtained using the electro-deposition technique by selecting urea and methanol as electrolyte. Chen et al. [18] have reported that the hydrophobic properties of the DLC film was promoted by doping fluorine using the electrolyte of methanol and 2,2,2-trifluoroethanol solutions. From the above-mentioned, the development of diamond-like carbon films prepared by electrochemical technique is the doping, and the expanding function of DLC film besides the traditional application in protective coating, micro-electromechanical devices, etc. Thus, we attempt to dope phosphorus into DLC film. Phosphorus could be easily deposited on the electrode surface via the electrolysis of triphenylphosphorus (PPh₃) dissolved into methanol because triphenylphosphorus could be readily polarized at high voltage. So, it is reasonable to achieve the co-deposition of phosphorus and carbon through electrolysis although the deposition of P-DLC films by an electrochemical route has not been reported up to now.

In this letter, we firstly synthesized P-DLC films by electrochemical technique. The surface morphology and micro-structure of the P-DLC films were investigated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. And their growth mechanism was also discussed.

2. Experimental details

P-DLC films were prepared in an electrolytic cell system reported elsewhere [18]. A $30 \times 10 \times 0.3 \text{ mm}^3$ silicon (100) substrate with a resistance of $7\text{--}13 \text{ }\Omega/\text{cm}^2$ was mounted on the graphite electrode. A platinum plate mounted on the graphite electrode, 6 mm away from the negative electrode, was used as the counter electrode. A mixture solution of methanol and Triphenylphosphorus (PPh₃) with mole ratio of 1000:1 was used to prepare P-DLC films, and the water tank temperature was controlled in the range of 45–50 °C. Before the deposition process, the silicon substrates were sequentially cleaned in 5% HF, deionized water and acetone in the ultrasonic bath. DC power with voltages of 800 V was applied in the deposition process the deposition duration was 10 h. In order to make clear

the change of the structure of carbon films after doping phosphorus, comparative DLC deposition without PPh₃ in CH₃OH solution was also carried out with DC voltage of 1200 V under the same conditions. During the deposition process, the current density of methanol-triphenylphosphorus solution under the voltage of 800 V gradually increased at the initial moment from $13.3 \text{ mA}/\text{cm}^2$ to $53.3 \text{ mA}/\text{cm}^2$, then the current decreased slightly with the deposition time. While the current density of methanol solution under the voltage of 1200 V displayed the similar tendency, but the current density ranged from $11 \text{ mA}/\text{cm}^2$ to $13.3 \text{ mA}/\text{cm}^2$, it also decreased with the deposition, which was lower than that of methanol-triphenylphosphorus solution.

The thickness of the as-deposited films was measured by the surface profiler. The surface morphology of the P-DLC films was observed with atomic force microscopy (CSPM4000), using “constant-force” mode and a Si₃N₄ tip. The XPS measurements on the composite films were performed on Perkin-Elmer PHI-5702 multi-functional X-ray photoelectron spectroscope, using Al K α radiation as the excitation source. Raman spectroscopic measurements were carried out to investigate the structure of the composite carbon films on a HR800 Raman spectrometer, operating with an Ar⁺ laser of 532 nm.

3. Results and discussion

XPS is a powerful tool to probe the composition of the carbon film and to investigate the chemical environment of the bonds. For the pure carbon film prepared at 1200 V, the C_{1s} spectrum was deconvoluted into three peaks: C=C (284.7 eV), C–C (285.5 eV) and C–O (288.9 eV), shown in Fig. 1. The ratio of sp³/sp² of the pure carbon film is 1.0, from the Gaussian curve-fitted C_{1s} spectrum. In the P-DLC films, the P/C atom ratio is 3.4%, calculated from the XPS analysis by computer (shown in Fig. 2). Likewise, on the assumption that the P-DLC films

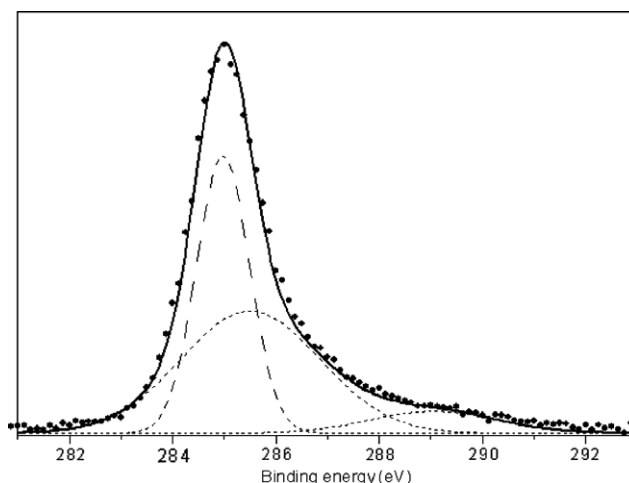


Fig. 1. The curve-fitted XPS spectrum of C_{1s} of the pure carbon film.

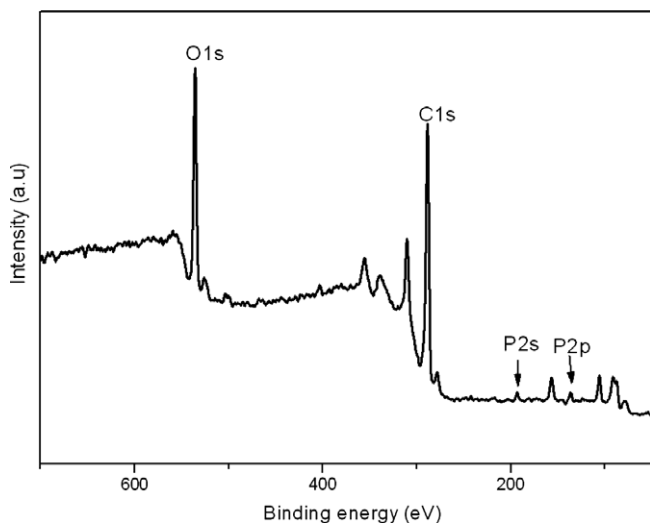


Fig. 2. The XPS spectra of P doped DLC film.

contained relatively little C–P bonding, the C_{1s} peak could be deconvoluted into C=C (284.9 eV), C=P (283.7 eV) [19], C–C (285.2 eV), and C–O (288.4 eV) bonding, and the ratio of sp^3/sp^2 of the P-DLC films from the Gaussian curve-fitted C_{1s} spectrum is 0.89, which is lower than that of pure carbon film. The deconvolution of the P_{2p} line for the same sample, shown in Fig. 3, gave three peaks at 132.4 eV, 130.9 eV, and 135.2 eV, assigned to C=P, C–P, and P–O bonds, respectively [19–21]. Because P_{2p} peak is composed of two different spin-orbit components, it indicated that the high-energy wing is related to P–O and C=P bonding [22]. The XPS analysis indicated that phosphorus have been successfully incorporated into the carbon film and mainly bonded to the carbon atoms in the form of C=P, and the concentration of sp^2 carbon phase was higher than that of pure carbon films. Furthermore, it indicated that the P impurity disturbed the tetrahedral amorphous network of the carbon films and enhanced the composite carbon films graphitization, which is in agreement with the report by Golzan et al. [5]. The P-DLC and DLC films were also characterized by Raman spectroscopy as shown in Fig. 4. For the P-DLC film deposited at 800 V, two broad bands appeared at 1360 cm^{-1} and 1590 cm^{-1} , typical signal of disordered carbon dominated by microcrystalline graphitic inclusions denoted by D and G bands, respectively [23,24]. Both peaks were observed in the Raman spectra of several types of allotrope such as microcrystalline graphite [25], and fullerenes [26]. However, for the pure carbon film deposited at 1200 V, besides the D and G bands there was another band around 1450 cm^{-1} that is assigned to the symmetrical deformation frequency of C–CH with sp^2 -hybridized C–C bonding [27] or a sp^3 -bonded diamond precursor phase [28]. Rerrari and Robertson [23] found the relationship between the visible Raman spectra and the sp^3 fraction in amorphous carbon films, which was that the sp^3 content increased with the simultaneous of G-peak position lowering and I_D/I_G ratio decrease. The intensity ratio of I_D/I_G of the DLC and

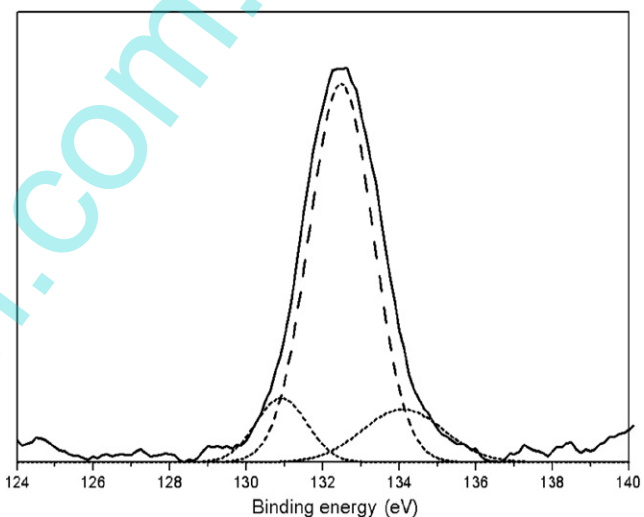
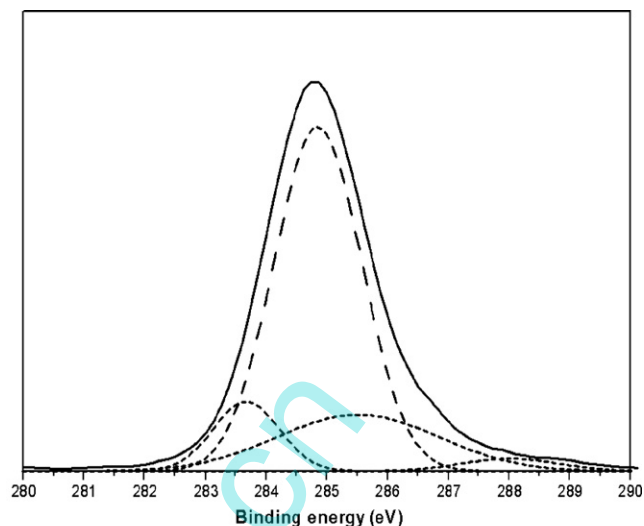


Fig. 3. The curve-fitted XPS spectra of C_{1s} and P_{2p} of the P-DLC film.

P-DLC film from the Gaussian curve-fitting Raman spectrum were 0.56 and 1.10, respectively, suggesting that the sp^3/sp^2 ratio decreased with the phosphorus doping, and a graphite-like structure dominated the P containing carbon film, which agreed with the XPS analysis. Fig. 5.

The thickness of the P-DLC film was about 800 nm measured by the surface profiler. AFM observations of the P-DLC films showed that P-DLC film exhibited a rougher surface with the RMS roughness of 16 nm than that of the DLC film with the RMS roughness of 5 nm, which may be related to the phosphorus incorporation into carbon matrix that disturbed the uniformity of carbon atoms, and roughened the surface of the composite carbon films.

During the vapor deposition process the formation of CP species was important for the preparation of phosphorus doped films [9,10]. The molecules of the $\text{CH}_3\text{OH-PPh}_3$ system contained both the electron-donor groups (CH_3^+ and P^{3+}) and the electron-acceptor groups (OH^- and Ph^-), and the dipole moments of the molecules were enhanced

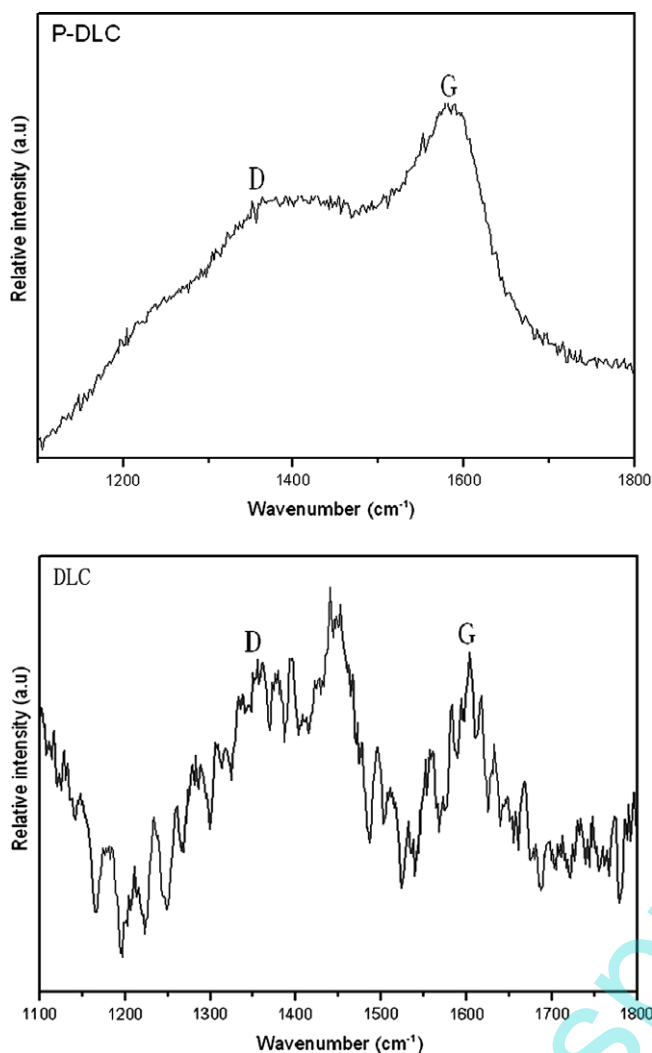


Fig. 4. The Raman spectra of P-DLC film and DLC film.

under a high potential. Moreover, the temperature of the tank played an important role for the methyl group produced under a high potential. Some reported that a certain amount of CH_3^+ would be produced under the high direct current potential when the temperature was above 42°C although the bond between CH_3O^- and H^+ was weaker than that of CH_3^+ and OH^- in the view of the chemistry [29]. In addition, it was noted that the current density of $\text{PPh}_3\text{-CH}_3\text{OH}$ solution was higher than that of pure methanol solution, which indicated that the ionization reaction could occur under a high potential. So we supposed that the growth process of P-DLC film in the liquid may be similar to the plasma deposition [30], and the main reactions for the formation of P-DLC film possibly occurred as follows: due to the low electro-negativity of the methyl and phosphorus groups and the enhanced dipole moment of the $\text{CH}_3\text{OH-PPh}_3$ solution under a high potential, some molecules must be ionized and a certain amount of methyl and phosphorus cations have been generated, thus, these cations were transferred to the negative electrode (substrate) under the applied potential. Furthermore, the reac-

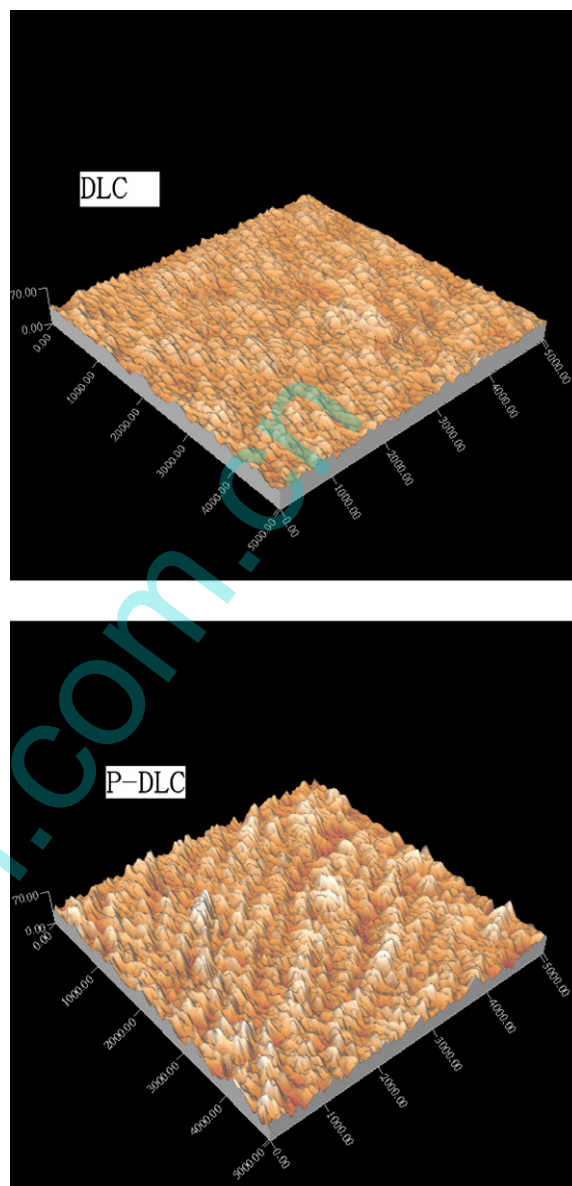
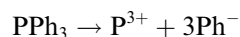
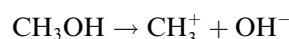


Fig. 5. AFM images (3D) of DLC and P-DLC film.

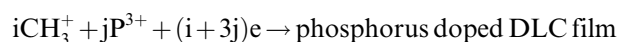
tion of the CH_3^+ and P^{3+} groups on the substrate surface occurred and produced the cross-linking CP species, which resulted in the formation of P-DLC film.

Based on the above discussion, phosphorus doped DLC film could be electrodeposited under high voltage, and its growth was speculated as the following schemes:

- (1) The ionization of CH_3OH and PPh_3 under a high potential in the liquid-phase:



- (2) The positive ion of CH_3^+ and P^{3+} were transferred to the negative electrode and reacted with each other:



As for the mechanism of the electrode reaction and the carbon film deposition process is complex and not clearly understood, in brief, more evidential data and experiments combined with other techniques are important for further investigating it.

4. Conclusions

In summary, we firstly synthesized phosphorus containing DLC films using the electrochemical deposition method. Phosphorus was mainly bonded to carbon atoms in the form of C=P and enhanced the carbon film graphitization indicated by XPS and Raman analysis. The formation mechanism of the P-DLC films was focused on the decomposition of methanol and PPh₃ to allow the formation CH₃⁺ and P³⁺, CP species were produced to form phosphorus carbide network.

Acknowledgements

This work is supported in financed by National Natural Science Foundation of China (NSFC) with Grant No. 50572108, No. 50772115 and the “Hundreds Talent Program” of Chinese Academy of Sciences.

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