



Field emission properties of DLC and phosphorus-doped DLC films prepared by electrochemical deposition process

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ABSTRACT

Field emission behavior of diamond-like carbon (DLC) and phosphorus-doped DLC (p-DLC) films prepared by electrochemical deposition process was comparatively investigated. It was shown phosphorus incorporation in the DLC film could lower the turn on field from 12 to 9.5 V/ μm and increase the current density from 12.6 to 45.7 $\mu\text{A}/\text{mm}^2$ under high electric field. And better field emission performance of p-DLC films would be mainly attributed to the influence of the surface morphology and the changes of microstructure due to the phosphorus incorporation.

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1. Introduction

Electron field emission from carbon-related materials, such as a-C:H films, a-C films, called diamond-like carbon (DLC) films, has been received considerable attention to develop the cold electron emitter materials for flat panel display in the microelectronic devices owing to its low surface work function [1]. Moreover, such super physical properties as high hardness, good wear resistance, excellent chemical inertness, high thermal conductivity, etc., were analogous to these of diamond, which indicates that DLC films could be used as the potential field emitter devices. In the case of the previous reports, the threshold fields of the pure DLC film were usually 3–20 V/ μm [2–4] and decreased to 1–12 V/ μm after nitrogen incorporation [5–7]. Thus, by comparison with DLC films, introduction of n-type impurity into DLC films could improve the field emission performance due to its providing electrons to close to the conduction band [8]. While the investigation on electron field performance of phosphorus-doped DLC (p-DLC) film was relatively few. Previously, phosphorus has been mainly used as n-type impurity in silicon [9], so it would be a promising alternative material to nitrogen in the carbon films. In addition, the resistivity of carbon films could decrease by 6–7 orders of magnitude after the incorporation of P with a content of only 1% [10]. Golzan et al. [11]

also reported that the addition of phosphorus in the carbon film could destabilize the tetrahedral network and be favorable to form sp² bonded network. Based on the first principle, when the concentration of phosphorus reaches to a certain extent, phosphorus carbide by analogy with the widely studied carbon nitride phase could be formed, reported by Claeysens et al. [12].

Previously, phosphorus-doped carbon films were mainly fabricated by vapor deposition techniques, such as plasma immersion ion implantation and deposition [13], capacitively coupled radio frequency plasma deposition [14], filtered cathodic arc method [10], pulsed laser deposition [15], etc. However, the process using electrochemical deposition was particularly interesting. Since electrochemical deposition technique had a low deposition temperature, atmospheric pressure, and simple experimental apparatus when compared with the vapor deposition processes. Accordingly, the fabrication of p-DLC film via the liquid electrochemical approach was realized in our previous work [16]. Numerous mechanisms of the emission performance of carbon films have been proposed and further supported by many corresponding experiments, such as negative electron affinity, defects bands in diamond, space charge induced band bending, surface states and surface dipole [17–20]. However, the mechanism for electron field emission from phosphorus-doped carbon films was poorly known, and study on field emission of p-DLC films was of significance.

Here we investigate electron field emission characteristics of p-DLC films fabricated by the electrochemical deposition process.

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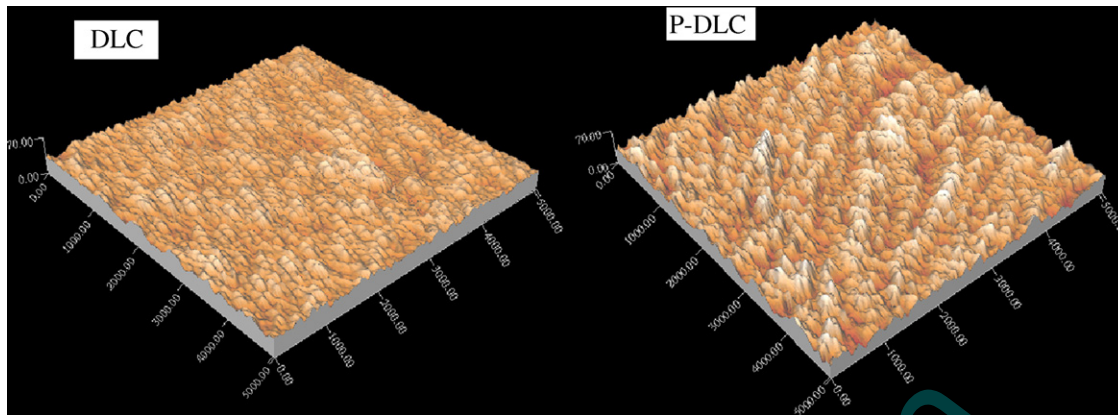


Fig. 1. The surface morphology of DLC and P-DLC composite films.

The aim of this work was mainly to clarify the relation of the morphology and microstructure of the as-deposited films with the electron field emission performance of p-DLC film.

2. Experimental details

DLC and p-DLC films were prepared in an electrolytic cell system reported by [16]. A silicon n(1 0 0) (1 cm × 2 cm) substrate with a resistance of $\sim 7\text{--}13 \Omega/\text{cm}^2$ was mounted on the negative electrode. A counter graphite electrode was kept 6 mm away from the negative electrode. A mixture solution of analytically methanol and triphenylphosphorus (PPh_3) 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, silicon substrates were sequentially cleaned 5% HF, distilled water and acetone in the ultrasonic bath. DC power with a voltage of 800 V was applied during the deposition process, and the deposition duration was 10 h. In order to make clear the influence of phosphorus incorporation on electron field emission of DLC films, DLC films prepared by electrolysis of analytically methanol with a voltage of 1200 V was followed the above-mentioned conditions.

The surface profiler was used to measure the step height between the substrate and the covering layer using a stylus scan the slope of the covering layer from the substrate in contacting mode [21,22], and the thickness of the as-deposited DLC and p-DLC

films measured was around 800 nm. The morphologies of DLC and p-DLC films were observed by CSPM4000 atomic force microscopy (AFM), using “constant-force” mode and a Si_3N_4 tip, as shown in Fig. 1. The fraction of P incorporated into DLC film, characterized by PerkinElmer PHI-5702 multi-functional X-ray photoelectronic spectroscopy (XPS) with an excitation source of Al K α radiation, was around 3%. A further investigation on the as-deposited films structure was performed on a HR800 micro-Raman spectroscopy using 532 nm Ar^+ laser.

The field emission properties of DLC and p-DLC films were tested by the conventional diode method [23] at an ambient pressure of $\sim 10^{-5}$ Torr. The anode consists of a rounded stainless steel panel with an area of 4.26 mm² whereas the as-deposited samples serving as cathode, and an anode–cathode spacing of 100 μm . The electric field is defined using a formula $E = V/d$ (V is the applied voltage and d is anode-to-cathode separation). The field emission current density is defined using the formula $J = I/S$ (I is the field emission current and S is the entire arc of samples exposed to the anode screen).

3. Results and discussions

3.1. Experimental results

The surface morphology of DLC and P-DLC film was characterized by atomic force microscopy (AFM). As evidence in Fig. 1 that p-DLC exhibited a relatively rougher surface with the RMS roughness of 16 nm than that of the DLC film with the RMS roughness of 5 nm, which might be attributed to the inhomogeneity of film-forming after phosphorus doping during the deposition process. Moreover, much more micro-protrusions existed on the surface of p-DLC film when compared with that of DLC.

Fig. 2 exhibited the Raman spectra of DLC and P-DLC films. The main feature between 1100 and 1800 cm^{-1} was D band and G band, indicating the amorphous nature of DLC and P-DLC composite film. In our previous published work [16], the investigation on the microstructure has been discussed in detail. Compared with DLC film, it was clearly observed that the increase of the I_D/I_G ratio and the up-shift of the G band in the Raman spectra, indicating the conversion from sp^3 to sp^2 carbon after phosphorus doping into carbon film, which might originated from an increase of sp^2 C or sp^2 C–P content and a simultaneously decrease of sp^3 C in p-DLC composite films. Consequently, most phosphorus atoms would be preferred to bond with carbon atoms in sp^2 hybridization, as shown in Fig. 3, which was beneficial to improve the conductivity of carbon film. In addition, from the curve-fitted XPS spectrum of P2p of P-DLC film shown in Fig. 3, it

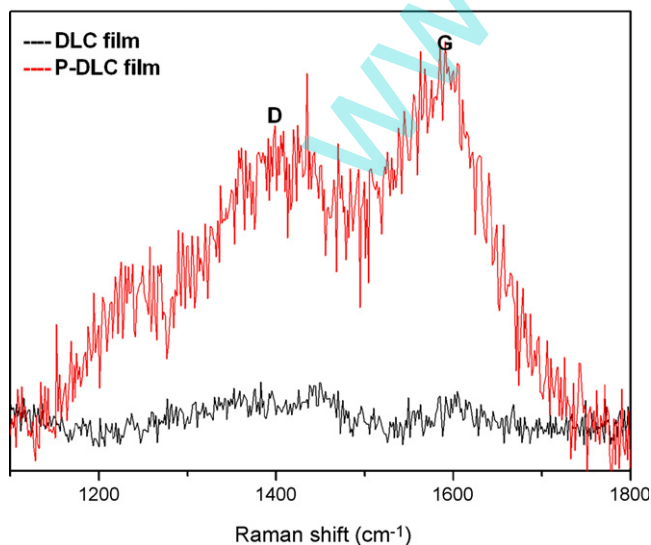


Fig. 2. Raman spectra of DLC and P-DLC composite films.

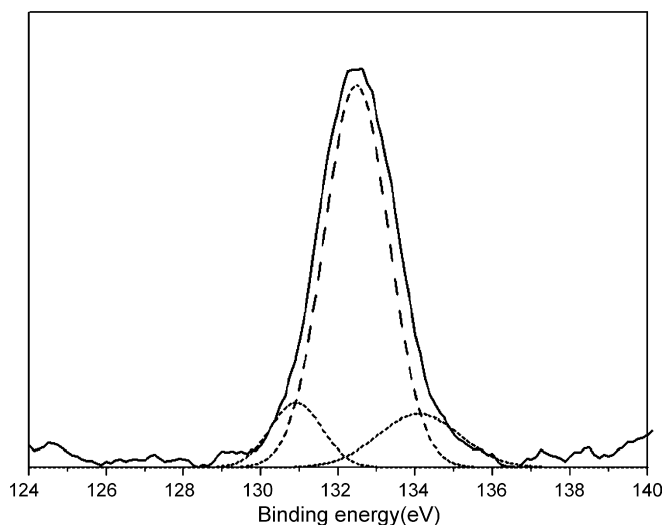


Fig. 3. The curve-fitted XPS spectrum of P2p of the P-DLC film.

suggested a fraction of phosphorus on the surface was oxidized owing to its exposure to air, which might further influence field emission behavior of P-doped DLC films.

Fig. 4a and b exhibited typical J - E characteristics of field emission from DLC and p-DLC films and the corresponding F - N curve, respectively. In previous reports, the threshold fields of pure a-C and diamond films were 3–20 V/ μm [2–4]. The threshold field obtained in this work was comparatively lower, and as shown in Fig. 4a that the threshold field was 12 V/ μm for DLC film while it was 9.5 V/ μm for p-DLC film, and the maximum current density was increased from 12.6 to 45.7 $\mu\text{A}/\text{mm}^2$ after phosphorus incorporation. So it can be concluded that the incorporation of phosphorus significantly lowered the turn-on field and simultaneously increased the current density of DLC film. After testing, the surface of as-deposited films was not damaged further observed by the optical microscope.

The Fowler–Nordheim (FN) curves of DLC and p-DLC films, plotting $\ln(J/E^2)$ vs. E^{-1} , were displayed in Fig. 4b. The conventional F–N equation was characterized of the electron emission through the surface potential barrier under the external applied field [24]:

$$J = A(\beta E)^2 \exp\left(\frac{-B\Phi^{3/2}}{\beta E}\right), \quad (1)$$

where J represented the emission current density in $\mu\text{A}/\text{mm}^2$, E represented the electric field in V/m, while Φ was the work function in eV, and β was the field enhancement factor at sharp geometry, $A = 1.4 \times 10^{-2}$, and $B = 6.8 \times 10^9$. Normally, there were two key factors, β and Φ , influenced field emission behavior of the solid-state film. Assuming that the field enhancement factor β was 1, the slope of the F–N curves would be $-B\Phi^{3/2}$. In Fig. 4b, the slope of DLC film was -53.40 under high field and -154.06 under low field, respectively. While for p-DLC film, the F–N plot was composed of three intersecting lines, where one slope under high electric field was -63.09 , -133.55 for the medium electric field and 20.42 for the low electric field. Consequently, the corresponding work functions of DLC film were calculated: 0.04 and 0.0801 eV, respectively. While the work functions of p-DLC film were 0.044, 0.0728 and 0.0208 eV, respectively. Actually, the work functions of carbon films were 3.5–4.0 eV confirmed by photoelectron measurements [21], so the field enhancement ($\beta = 1$) was of underestimation, the real values of the work functions could be

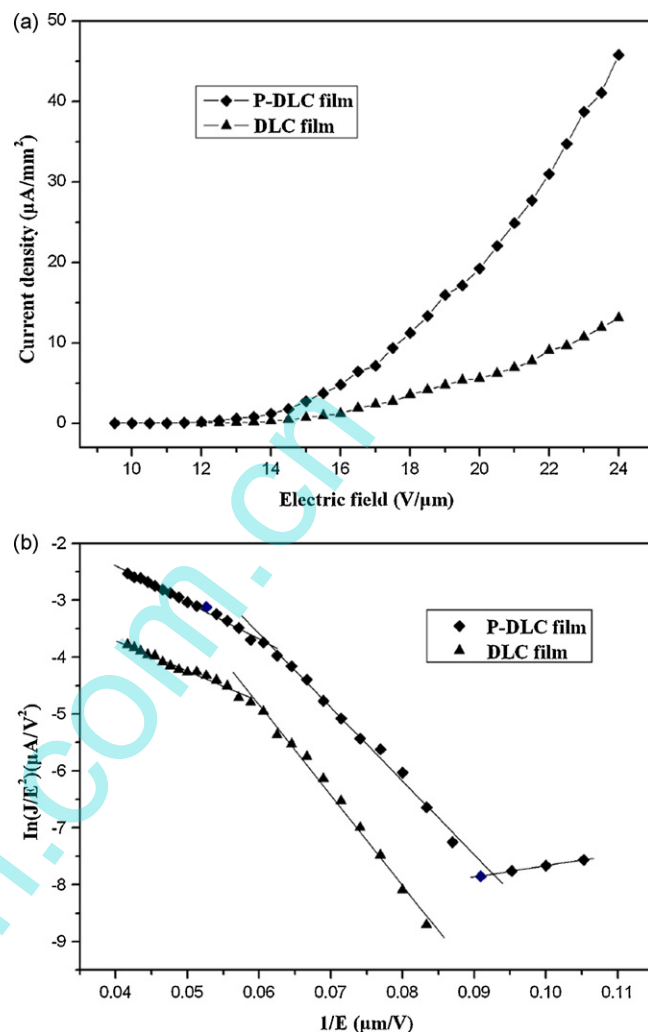


Fig. 4. (a and b) Typical field-emission characteristics of DLC and P-DLC film.

larger than that of the calculation. Xu et al. [25] considered that experimental data could not be fitted better, which was similar to this work shown in Fig. 4b, therefore the derived values of Φ and β were inconvincible. Their work also confirmed that an F–N transition of with the nonlinearity resulted from thermionic emission (TE) at low electric field to field emission (FE) at high electric field, which was also observed in our work, both for DLC and p-DLC films. But at the relatively low electric field, field emission mechanism of p-DLC film was different from that of DLC film, and the similar F–N plot could also be observed in vertically aligned CNTs [26]. Although phosphorus incorporation could improve the field emission performance of the DLC films, the mechanism of field emission was still debatable. So the following discussion mainly focused on the relationship of field emission behavior and the microstructure, surface morphologies of the as-deposited films.

3.2. Discussion

From the experimental results of field emission testing, it has been shown that introduction of phosphorus improved the field emission behavior of the DLC films, but the mechanism of field emission was worth discussing. The following discussion of the field emission mechanism was mainly on the basis of the F–N

equation, the microstructure and the morphologies change of films prepared by electrochemical deposition.

In the F–N equation, there were two noticeable factors: β and Φ . Thereinto, one key parameter β , called the field enhancement factor, which was related to the geometry of the emitters and the ambient environment. Distinctly, some protrusions were observed after introduction of phosphorus into DLC films shown in Fig. 1a and b. It has been reported that the field emission performance was dependent on the nanostructured protrusions or tips with a high emission enhancement [27,28]. Therefore, the electrochemical deposition process created some protrusions with high-localized electric fields on the surface of p-DLC film, which would make great contributions to the key parameter β and further lower the turn-on electric field. Additionally, From Fig. 4a, it could be observed that the current fluctuation was high in the medium and low applied voltages range, called the hysteresis effect which could be explained as follows: because these protrusions have an inherent inertia to remain stacked with the increasing external electric field, only its intensity decreased, leading to the current emission remained high at medium electric field compared to that at low electric field. That might lead to the bend of the F–N equation of P-DLC in the medium and low applied voltages range.

Besides the influence of the surface morphology, the composition and the internal structure played a significant role in field emission behavior. While in the case of Φ , it was closely associated with the microstructure and composition as well as the field enhancement factor β . From the calculated results of the work functions, it was found that incorporation of phosphorus moderately reduce the effective work function under high electric field, indicating that phosphorus might be a shallow donor in the DLC film. Moreover, phosphorus, the n-type impurity, had the potential to enhance the electron field emission properties, such as in doped diamond or nanocrystalline carbon films by providing electrons close to the conduction band [29,30]. So incorporation of phosphorus might make the Fermi-level shift to the conduction band in p-DLC film. From another standpoint, pure DLC films with bad conductivity generally exhibited unsatisfactory field emission performance [18]. When phosphorus was incorporated into DLC films, the fraction of sp²-hybridized C–C and C–P bonds increased, indicating that phosphorus doping enhanced carbon film graphitization, which was beneficial for the conduction, in other words, more sp² clusters was embedded in the insulating sp³ matrix in p-DLC film, confirmed by Raman analysis and XPS. These sp² clusters-forming caused electron delocalization and/or improved electron hop between the clusters. Moreover, these clusters were likely to be overlapped, which also further accelerated electrons transportation between the connecting clusters [31]. The electrons would be easily extracted from the film surface while the external electric field was applied.

Phosphorus incorporation not only increase the conductivity of carbon films, but also simultaneously introduced a number of defects in carbon films, such as vacancies, dislocations and stacking faults, which might have an important effect on field emission behavior [32,33]. Moreover, the defects with the electronic states could be formed, causing one or more sub-bands within the sp³ carbon band gap [34], which was convenient for emitting electrons into vacuum from these bands and/or being transported to the surface states for emission. Essentially, the Fermi level was elevated by these defects and their associated electronic structures, and the electron could tunnel through the reduced energy barrier.

Further, in the case of the theoretical calculation of p-DLC films [35], a range of different content of p-DLC film was examined, indicating both defective diamond-like and graphitic-like structures in the composite films. And the more defects in diamond-like

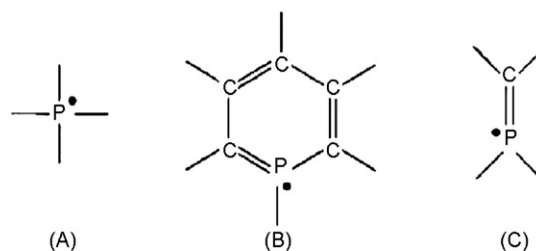


Fig. 5. Possible bonding forms of phosphorus in P-DLC film.

carbon, the better the emitter, reported by Zhu et al. [36]. Some reports based on experiments results also confirmed phosphorus bonding by the theoretical calculations [37]. And if phosphorus was mainly bonded to carbon in the forms of C–P and/or C=P, which would provide the single electrons in favor of field emission behavior, it might be similar to nitrogen containing carbon films [38]. Based on Refs. [35,37,38], it was believed that phosphorus was bonded to carbon atoms in various forms, but these structures as shown in Fig. 5, to a great degree, might have a positive effect on field emission behavior. Whereas Claeysens et al. [12,39] reported phosphorus atoms incorporated into DLC films were preferred to bond with carbon atoms in the sp³ hybridization on the basis of the plane-wave density functional theory (DFT) and periodic numerical atomic orbitals density functional theory in different modes. Of course, some fraction of phosphorus was bonded to carbon atoms, forming C–P bonds confirmed in this work. There still were some contradictions on the phosphorus bond forming in the films and field emission mechanism of p-DLC film. Therefore, the better understanding of such phenomenon should be followed by researches confirmed by experiments and further theoretical calculations.

4. Conclusion

Field emission behaviors of DLC and p-DLC films fabricated by electrochemical deposition process were studied. It exhibited that phosphorus doping into DLC film could lower the turn-on field and simultaneously increase the current density under high electric field, showing better field emission performance. It was believed that p-DLC film would have a potential advantage for field emission applications in flat panel displays and vacuum micro-electronics.

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