Research Article

Evidence of Carboxyl Modification of Hydrogen-Free Diamond-Like Carbon Films Assisted by Radio Frequency Plasma in Vacuum

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Modification of hydrogen-free diamond-like carbon (DLC) is presented, with acrylic acid (AA) vapor carried into a vacuum chamber by argon and with the in situ assistance of low-power radio frequency (RF) plasma at a temperature below 100°C. Measured by atomic force microscopy (AFM) technique, the roughness (Ra) of the DLC was 1.063 ± 0.040 nm. XPS and FT-IR spectra analysis showed that carboxyl groups were immobilized on the surface of the DLC films, with about 40% of carboxyl group area coverage. It was found that the RF plasma and reaction time are important in enhancing the modification rate and efficiency.

1. Introduction

Diamond-like carbon (DLC) films, which are hard, stable, inexpensive, and biocompatible, have been widely used in the fields of biosensors and electrochemistry for many years [1, 2]. With the development of modification technology, DNA and protein have been immobilized on DLC films [3, 4]. In the future, DLC films are promising in the applications of electrodes and bioactivity protected films in biosensors. To do so, one challenge is to improve carboxyl or amino modification techniques for the DLC surface to improve protein or DNA immobilization covalently. Recently, a photochemical functionalization technique was carefully studied, which makes possible a functionalized organic monolayer by UV light irradiation immobilization on the hydrogen-terminated surfaces of the nanocrystalline and single-crystal diamond (111), in a thin layer of liquid reactants [5, 6]. However, this technique requires hydrogen-terminated DLC surface at a temperature higher than 800°C (to remove the surface oxygen [7]), which is too high for some applications, such as GMR biosensors, and would damage the GMR elements [8]. Furthermore, the functionalization time was always over 10 hrs to obtain a functional group coverage of 10% [6, 9] (for the trifluoroethyl ester of ω-undecenoic acid (TFU), and the coverage is defined by the ratio of carboxyl group content over that of the carbon monolayer on the surface of the DLC). Ababou-Girard et al. [10] reported a thermal functionalization method to graft ethyl undecylenate molecules onto the hydrogen-terminated amorphous carbon surface. However, this method showed a poor efficiency, with obtained DLC:H rate of merely 4%.

Hovis et al. [11] found that vinyl group (C=C) would react with hydrogen-free diamond surface in ultravacuum (1.33 × 10⁻⁸ Pa) due to the active sites (dangling bands [12], surface π bonds [11], etc.) on the surface of hydrogen-free diamond. However, the reaction rate for vinyl groups is about the order of 10⁻³ on diamond, in comparison to 1 on Si; the ultravacuum is not conveniently obtained.

In this paper, we studied the carboxyl modification on a hydrogen-free DLC surface, by introducing unsaturated
Figure 1: The AA-modification route of the DLC films.

Table 1: Sample-modification-process parameters, and the estimated coverage rate of the carboxyl groups based on XPS data.

| Sample | Step 1 RF power (W) | Step 2 Time (min) | Step 3 O/C (At.%) | Coverage (first method) | Coverage (second method) |
|--------|---------------------|-------------------|-------------------|-------------------------|-------------------------|
| S1     | √                   | —                 | —                 | 18.1%                   | —                       |
| S2     | √                   | —                 | √                 | 10.0%                   | <10%                    |
| S3     | √                   | 0                 | 60                | 15.7%                   | 23%                     |
| S4     | √                   | 20                | 10                | 19.9%                   | 44%                     |
| S5     | √                   | 20                | 60                | 18.8%                   | 40%                     |
| S6     | √                   | 20                | 60                | 18.8%                   | 60%                     |
Figure 2: X-ray photoelectron spectroscopy (XPS) C1s spectra, for the original DLC film (dots, S1), the surface hydrogenated DLC (square, S2), and the AA-modified DLC film with RF power of 20 W (triangle, S5) (a), which are normalized to a total intensity of 50000; that for AA-modified without RF plasma assistance (S3) for 60 min (b); that for AA-modified with RF power of 20 W (S5) for 60 min (c). The fitted curves are deconvolved into sp² carbon at 284.7 eV, sp³ carbon at 285.5 eV, C–O at 286.4 eV, C=O at 287.3 eV, and –COOH at 288.5 eV.

3. Results

3.1. The XPS Spectrum of Samples. The hydrogen-terminated DLC film could reduce oxygen and carbon dioxide in the air contamination, which benefits the analysis of the C1s spectra for the AA-modified DLC films (Figure 2(a)). Compared with the hydrogen-terminated DLC film (S2), the C1s spectrum of the AA-modified DLC (S5) has one more peak at the binding energy (BE) between 288.0 eV and 289.0 eV (Figure 2(a)). The O/C atom ratio for the hydrogen-terminated DLC (S2) is only 10%, while the AA-modified (S5) is 19.9% (see Table 1). The bulk C1s peaks of all the samples are deconvolved into two components: the sp² carbon at 284.7 eV and the sp³ carbon at 285.5 eV (Figures 2(b) and 2(c)) [14]. The difference of their binding energy was fixed at 0.8 eV [15, 16].

XPS C1s spectra were also used to analyze oxygen-bonded carbon species. The C1s spectra were fitted by Lorentzian-Gaussian curve (with L/G ratio of 20%). In comparison with the hydrogen-terminated DLC (S2), the C1s spectrum of the AA-modified DLC film (S5) shows a peak at around 288.5 eV (–COOH) and two small peaks at around 286.4 eV (C–O) and 287.3 eV (C=O) (see Figure 2(c)), which agrees with the reports [13, 17, 18] that the XPS C1s spectrum of oxygen-bonded carbon could be deconvoluted to 286.4 eV, 287.4 eV, and 288.5 eV, which corresponded to ether or alcohol (C–O) carbon atoms, ketone (C=O) carbon atoms, and lactone or carboxyl (O–C=O) carbon atoms, respectively. The spectrum of the modified DLC films by AAs without RF assistance (S3) also exhibits three peaks at the bonding energy of 286.4 eV, 287.4 eV, and 288.5 eV (Figure 2(b)).
but the peak intensity at 288.5 eV is weaker than that of S5.

3.2. The FT-IR Spectra of the Samples. Compared to the sample of H-terminated DLC (S2), FT-IR spectra of the AA-modified samples (S4, S5) have two C=O stretching vibrations of 1736 cm\(^{-1}\) and 1718 cm\(^{-1}\) (Figure 3) [19]. The peaks at 1108 cm\(^{-1}\), 891 cm\(^{-1}\), and 613 cm\(^{-1}\) are Si–O–Si stretching vibration, Si–C stretching vibration, and Si–Si band, respectively [20]. The peaks at 1570 cm\(^{-1}\) are from the C=C stretching vibration of DLC film [20]. Figure 4 shows the IR spectra of the annealed film (at 200°C for 120 min) and the unannealed film (S5). The result indicates that acrylic acid is not condensed, nor absorbed on surface, but stably bound on the surface because the C=O stretching vibrations are mostly the same. Some very weak peaks at 1700–1600 cm\(^{-1}\) belong to H\(_2\)O in the air.

3.3. The AFM Image of Sample 1. The surface morphology of the DLC film (S1) was studied by AFM. The particle size in the film is about 25 nm on average, and the surface roughness \((R_s)\) is 1.063 ± 0.040 nm (see Figure 5 which shows the DLC film is a uniform, compact, and smoothness thin film.)

4. Discussion

The XPS and FT-IR indicate that the acrylic acid molecules have been immobilized on the surface of the DLC films. To identify the contribution of the carboxyl groups in the FT-IR spectra, it is necessary to exclude the interference of ketone and ester groups on the surface of the DLC films. On one hand, since the content of the ketone groups is just about 1/3 as that of carboxyl groups, the interference of the ketone groups can be excluded in the FT-IR spectra; on the other hand, the fact that the AA-modified samples (S4, S5) have no new strong absorption peak in the region of 1760 cm\(^{-1}\) to 1720 cm\(^{-1}\) associated with AA dimers, C=O in open-chain associations, and C=O in terminal unassociated carboxyl groups [21], respectively, we attribute the absorption bands of the sample (S4 and S5) at 1718 cm\(^{-1}\) and 1736 cm\(^{-1}\) to \(\text{C}=\text{O}\) and \(\text{C}^*=\text{O}\), respectively. Both C related to two adjacent carboxyl groups immobilized on the DLC films (Figure 6).

The rate of the carboxyl group coverage on the DLC films based on the C1s spectra data was estimated in two methods. The first method [18] was based on the assumption that all the carbon atoms on the DLC film surface are either oxidized by O\(_2\) or reacted with AAs. So the carboxyl group coverage is defined by the ratio of peak area of the carboxyl groups at 288.5 eV in C1s over that of the total species. Taking S5, for example, we estimated the rate of coverage in this way to be about 44%. The second method [10] was based on the assumption that only a single layer

![Figure 3: FT-IR spectra (4000 cm\(^{-1}\) ~ 400 cm\(^{-1}\)) for (S4) the AA-modified DLC film with RF power of 20 W for 1 h, (S5) the AA-modified DLC film with RF power of 20 W for 10 min, and (S2) the hydrogen-terminated DLC film. The insert is FT-IR spectra from 2000 cm\(^{-1}\) to 1200 cm\(^{-1}\). The absorption bands in the region of 1760 cm\(^{-1}\) ~ 1700 cm\(^{-1}\) are attributed to the C=O bonds in carboxyl groups and those in the region of 2000 cm\(^{-1}\) ~ 1780 cm\(^{-1}\) to the combination.](image3)

![Figure 4: FT-IR spectra of the annealed film and the unannealed film (S5). The spectrum presents the following information: C=C stretching vibrations (1740 and 1708 cm\(^{-1}\), 1736 and 1710 cm\(^{-1}\)).](image4)

![Figure 5: An AFM image (3D) of the DLC film (S1).](image5)
These results suggest that RF assistance could enhance the modification rate and efficiency. Such process is a new, mild, efficient, and inexpensive technique for the carboxyl group immobilization on the DLC films.

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