

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 (R_a) 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

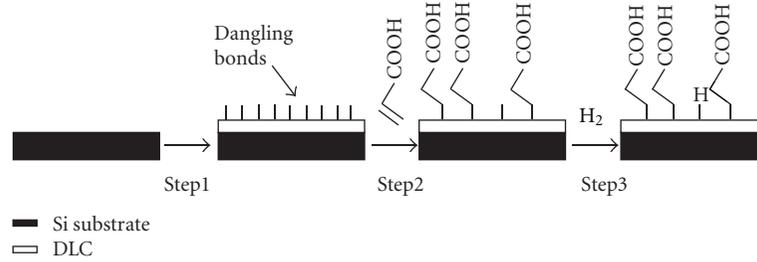


FIGURE 1: The AA-modification route of the DLC films.

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

Sample	Step 1	Step 2		Step 3	O/C (At.%)	Coverage (first method)	Coverage (second method)
		RF power (W)	Time (min)				
S1	✓	—	—	—	18.1%	—	—
S2	✓	—	—	✓	10.0%	<10%	<10%
S3	✓	0	60	✓	15.7%	23%	17%
S4	✓	20	10	✓	—	—	—
S5	✓	20	60	✓	19.9%	44%	43%
S6	✓	20	60	✓	18.8%	40%	60%

carboxyl acid vapor into a high vacuum chamber (at a base pressure of 2×10^{-3} Pa), where an RF plasma was used to enhance the modification rate and efficiency. The temperature of the DLC film was below 100°C before the in situ functionalization process. About 40% coverage of the carboxyl groups was obtained after a one-hour modification.

2. Experimentals

2.1. Sample Preparation. An RF-magnetron sputtering system was employed to deposit DLC films on Si (100) wafers (twin polished for FT-IR characterization, and single side polished for X-ray photoelectron spectroscopy). A $\phi 75$ graphite target (99.99% purity) was mounted 7 cm away from and in parallel to the Si wafer mounted on a rotatable substrate stage, which could bring the wafer into, or out of the plasma. The graphite target was presputtered for about 30 min to remove possible surface contaminations before deposition. The base pressure of the deposition chamber was 2×10^{-3} Pa. All the DLC films in this paper were deposited at an RF power of 120 W and in high-purity (99.999%) argon at a pressure of 3 Pa (± 0.2 Pa). After a deposition of 30 min, DLC films of 150 nm in thickness were obtained (Step 1 in Figure 1). The as-deposited DLC films were moved away from the centre plasma zone by the substrate stage, where, carried by argon (0.15 MPa), acrylic acid (AA, 99.5% purity, ACROS) vapor was introduced into the deposition chamber with a controlled pressure of 10 Pa in situ. The temperature of the liquid AA was about 30°C . The modification time was set to 10 min or 60 min with the RF power of 20 W (Step 2 in Figure 1). After the deposition or modification of the DLC films, the chamber was evacuated to 2×10^{-3} Pa; then when H_2 (99.99% purity) gas was introduced the chamber and the pressure will be fixed at 10 Pa for 60 min, with an RF power of 30 W (Step 3 in Figure 1). The sample temperature was

kept below 100°C . AA-modified DLC film was annealed at 200°C for 120 min in vacuum and then examined using FT-IR spectroscopy.

2.2. Characterization. The original (S1), H-terminated (S2), AA-modified DLC film without (S3), and with (S5) RF plasma assistance were all characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250), with a monochromatized $\text{AlK}\alpha$ source (1486.6 eV), and the base pressure was maintained at 2×10^{-7} Pa. The pass energy and the step size for survey scans were set to 100 eV and 1.0 eV, while the step size for narrow scans was set to 0.05 eV, respectively. All the samples were not cleaned by Ar^+ unless noted otherwise, and all the binding energies were referenced to the main $\text{C}1s$ peak (284.8 eV).

Infrared spectra were used to analyze whether the carboxyl groups were immobilized on the surface of the DLC films, since it was difficult for XPS to distinguish carboxyl groups from ester groups, even though XPS was a sensitive and reliable tool for quantitative analysis of the surface functional group composition [10, 13]. FT-IR (Nicolet 6700) was employed to investigate carboxyl modification efficiency for samples modified at 10 min (S4) and 60 min (S5). The hydrogen-terminated DLC film (S2) was also studied by the FT-IR in comparison with the carboxyl-modified samples. The number of scans was 64, while the scan step was 4 cm^{-1} . (The labels of the samples for characterization are summarized in Table 1.)

The surfaces of the DLC films was scanned by an atomic force microscope (AFM, SPI3800N, S II Seiko, Japan) under an ambient atmosphere at room temperature. The AFM measurements were performed in noncontact mode, and an area of $200\text{ nm} \times 200\text{ nm}$ was scanned at a scan rate of 2.99 Hz with 256×256 pixel resolution.

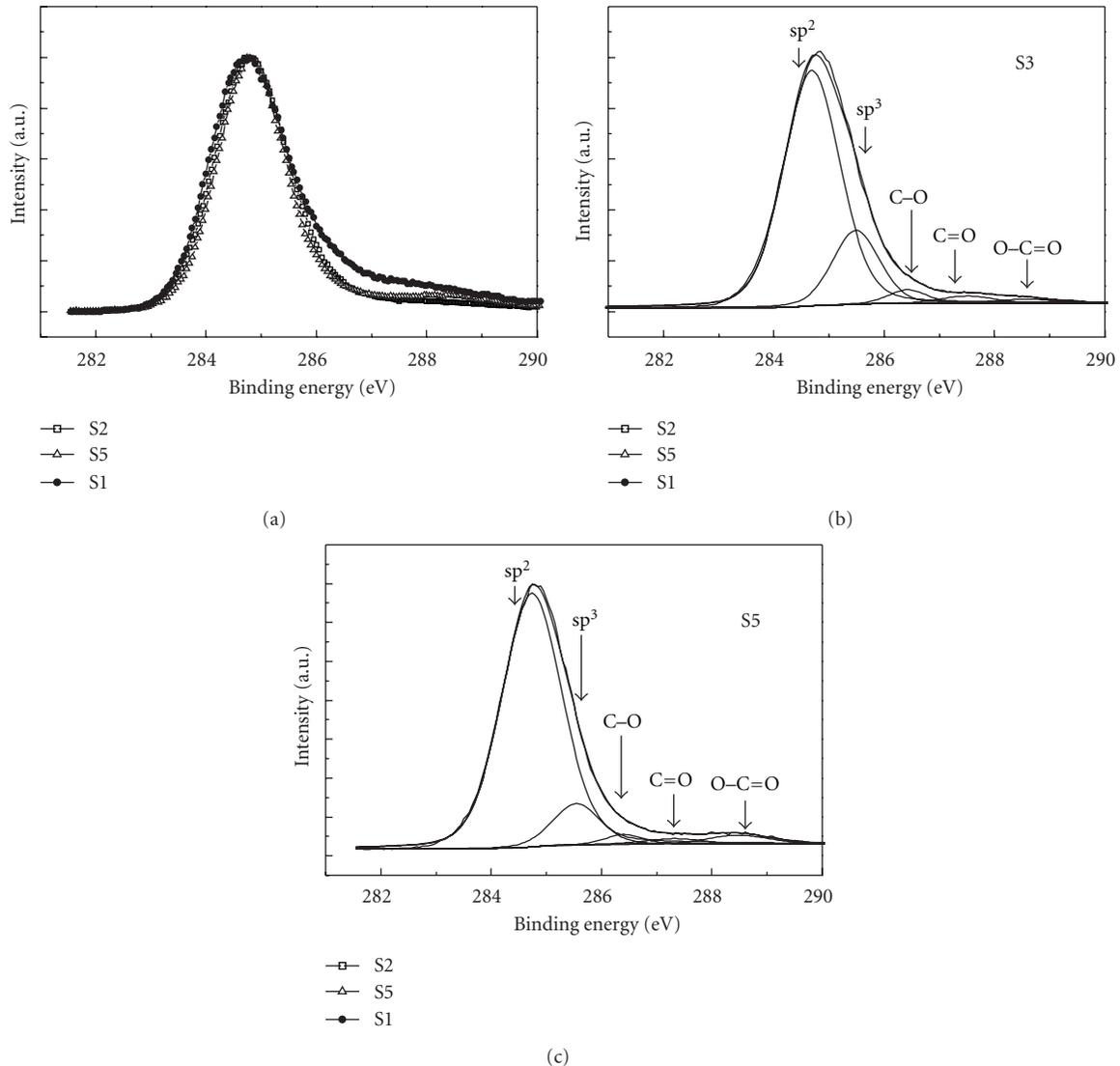


FIGURE 2: X-ray photoelectron spectroscopy (XPS) C1s spectra, for the original DLC film (dots, S1), the surface hydrogenated DLC (square, S2), and the AA-modified DLC film with RF power of 20 W (triangle, S5) (a), which are normalized to a total intensity of 50000; that for AA-modified without RF plasma 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 deconvoluted into sp^2 carbon at 284.7 eV, sp^3 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 deconvoluted into two components: the sp^2 carbon at 284.7 eV and the sp^3 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 $1700\text{--}1600\text{ cm}^{-1}$ belong to H_2O 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_a) is $1.063 \pm 0.040\text{ nm}$ (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 $1300\text{ cm}^{-1} \sim 1000\text{ cm}^{-1}$ (Figure 3), which is attributed to the C–O absorption band of the esters [20], suggests that the interference of the ester can also be excluded. In addition, comparing with the spectra of pure liquid AA, which has three characteristic absorption bands of carbonyl groups at 1695 cm^{-1} , 1724 cm^{-1} , and 1740 cm^{-1} , and attributed to 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

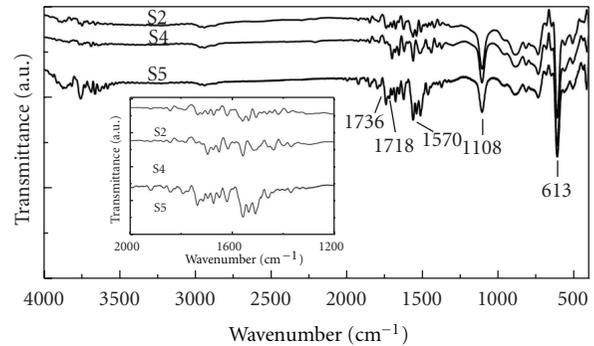


FIGURE 3: FT-IR spectra ($4000\text{ cm}^{-1} \sim 400\text{ cm}^{-1}$) for (S4) the AA-modified DLC film with RF power of 20 W for 1 h, (S5) the AA-modified DLC film with RF power of 20 W for 10 min, and (S2) the hydrogen-terminated DLC film. The insert is FT-IR spectra from 2000 cm^{-1} to 1200 cm^{-1}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

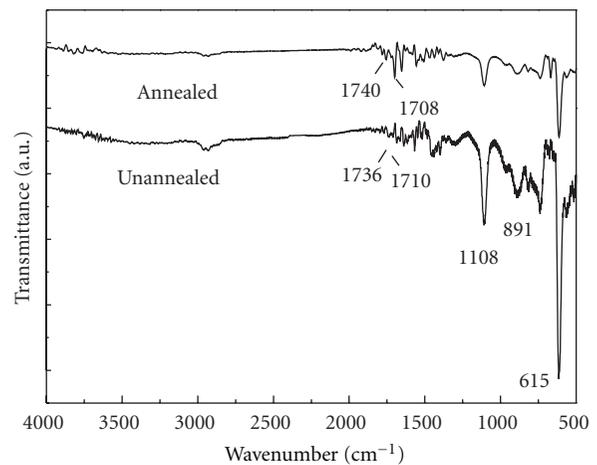


FIGURE 4: FT-IR spectra of the annealed film and the unannealed film (S5). The spectrum presents the following information: C=O stretching vibrations (1740 and 1708 cm^{-1} , 1736 and 1710 cm^{-1}).

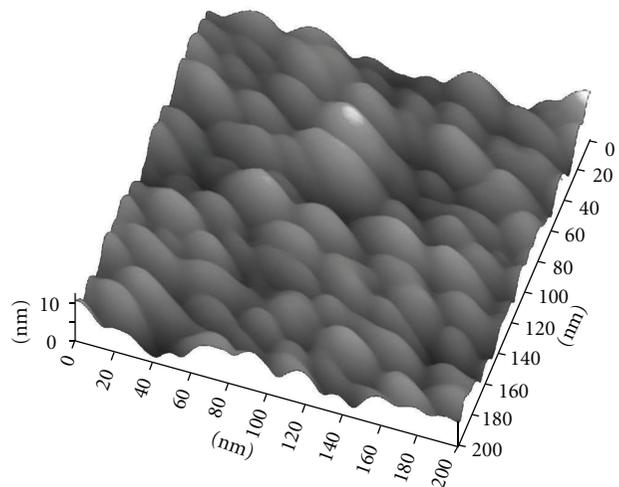


FIGURE 5: An AFM image (3D) of the DLC film (S1).

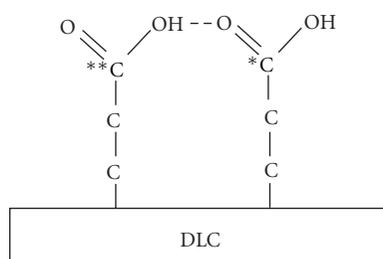


FIGURE 6: Associations formed by two adjacent carboxyl groups immobilized on the DLC film.

of carboxyl group is immobilized on the DLC surface, so that, the calculation of the carboxyl coverage should be constrained only to the surface carbon. This method is just a reference as a supplementary of the first method. By using $I = I_0 \exp(-d/\lambda)$, in which λ is the inelastic mean free path (IMFP), to estimate the contribution of surface monolayer carbon, the rate of carboxyl coverage was defined by the ratio of carboxyl group peak area over that of the carbon atom monolayer on the surface of the DLC film. The IMFP for C1s photoelectron of DLC was estimated by using $\lambda = \lambda_G C_{sp^2} + \lambda_D C_{sp^3}$, in which C_{sp^2} and C_{sp^3} are the atomic ratios of the sp^2 carbon and the sp^3 carbon in the total carbon atoms, respectively. The graphite IMFP λ_G was 2.24 nm, and the diamond IMFP λ_D was 1.4 nm [22]. Considering the thickness of the AA monolayer was about 0.4 nm, which is just about 1/9 of the IMFP for C1s photoelectrons in the compact organic layer [10], one could neglect the photoelectron inelastic scattering effect of the AA monolayer. Taking S5, for example, we estimated the carboxyl group coverage to be 43% in the second way. For sample S6, which was prepared in the same condition as that of S5, the coverage ratio was about 40% and 60% for the first method and the second method, respectively.

Furthermore, we studied the effect of the RF on assisting the modification process in the same methods. The carboxyl groups' coverage ratio for the AA-modified DLC film (S3) without RF assistance is just about 23% and 17% for the first method and the second method, respectively (Table 1). These results suggest that RF assistance could enhance the modification rate and efficiency, and that the coverage of the physically adsorbed AAs is significantly lower than the chemically bonded AAs (as those on S5).

Finally, the XPS analysis also suggests that the hydrogen termination is helpful for blocking impurity absorption on the DLC surface from the air, since the atomic ratio of O/C—of the hydrogen-terminated DLC film (S2) with RF assistance is much lower than that of the original DLC (S1). The active sites (such as dangling bonds) on the DLC surface terminated by the hydrogen can otherwise arrest oxygen atoms [7].

5. Conclusions

Assisted by low-power RF plasma, carboxyl groups were immobilized on the surface of the hydrogen-free DLC film deposited by RF-magnetron sputtering, as evidenced by XPS

and FT-IR spectra. The coverage ratio of the carboxyl groups estimated was possibly up to 40%. The low power RF plasma enhanced the modification rate and efficiency. Such process is a new, mild, efficient, and inexpensive technique for the carboxyl group immobilization on the DLC films.

Acknowledgments

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