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Structure and properties of fluorine and boron co-alloyed diamond-like carbon films

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Abstract

Fluorine (F) and boron (B) co-alloyed diamond-like carbon (FB-DLC) films were prepared on polymethyl methacrylate (PMMA), polycarbonate, glass, silicon (100) and Mo sheets by the plasma immersion ion processing (PIIP) technique. A pulse glow discharge plasma was used for the PIIP deposition and was produced at a pressure of 1.33 Pa from acetylene (C₂H₂), diborane (B₂H₆), and hexafluoroethane (C₂F₆) gas. The composition of FB-DLC films was measured by using the ion beam analysis techniques, and the bonding structure was characterized by IR and Raman spectroscopies. The co-alloying of F and B into DLC films resulted in the formation of F–C and B–C hybridized bonding structures. The levels of the F and B concentrations affected the composition, chemical bonding and properties as was evident from the changes observed in hydrogen concentration, optical gap energy, hardness, friction coefficient, and contact angle of water on films. Compared to B-alloyed or F-alloyed DLC films, the F and B co-alloyed DLC films exhibited a reduced hydrogen concentration, high hardness and optical gap energy, and improved hydrophobic and tribological properties.

1. Introduction

Diamond-like carbon (DLC) films are well known for their high hardness, low friction and wear, excellent optical and electrical properties, which makes them ideally suited for many applications in mechanical, electronic, optical, and other technological areas [1, 2]. Recently, research has shown that it is possible to prepare hydrophobic DLC films that are hard and have excellent optical properties [3–5]. The incorporation of fluorine (F) into DLC films has so far been the most effective way to improve the hydrophobicity, i.e. to increase the contact angle of the film to water [3–5]. A downside of adding F to DLC, however, is the reduction in hardness that occurs with increasing F concentration [3, 4]. On the other hand,

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other research that has examined the influence of alloying B into DLC films has shown that B incorporation suppresses the formation of sp^2 graphitic clusters, and results in an increase of the sp^3 bonding and thus hardness [6]. One downside of DLC alloying with B is that it results in an increase of hydrogen (H) concentration when DLC films are synthesized using a $B_2H_6 + C_2H_2 + Ar$ plasma [6]. However, since F alloying has been shown to be effective at suppressing H incorporation in DLC films [3–5], one may speculate about co-alloying B and F with DLC to produce films with a combination of high hardness and good optical and hydrophobic properties.

In our previous work, B-alloyed, F-alloyed, and F and B co-alloyed DLC films have been prepared by plasma immersion ion processing (PIIP) depositions with plasmas of $B_2H_6 + C_2F_6 + Ar$, $C_2F_6 + C_2H_2$, and $B_2H_6 + C_2F_6 + C_2H_2$, respectively [4, 6, 7]. The PIIP technique has been chosen for thin film deposition because it provides the technological benefits of ion beam assisted deposition and plasma source ion implantation, along with non-line-of-sight processing, making it well suited for modifying large-sized complex shaped commercial parts [8]. It was found that the incorporation of B_2H_6 and C_2F_6 into PIIP DLC depositions resulted in the formation of F–C and B–C hybridized bonding structures, which modified the DLC film with a reduced hydrogen concentration and stress, while maintaining a high hardness, low friction coefficient, and high wetting contact angle. In this paper, the PIIP technique was applied to synthesize F and B co-alloyed DLC (FB-DLC) films on the transparent substrates, with the intent of optimizing the effects of F and B co-alloying on the structure and properties of DLC coated optical materials. The hydrophobic and optical properties as well as hardness and tribological performance were studied with regarding to the chemical composition and bonding structure of the FB-DLC films.

2. Experimental details

The transparent optical substrates used for deposition of DLC film are glass and polymeric plates, such as polymethyl methacrylate (PMMA) and polycarbonate (PolyC). The DLC films were also prepared on silicon (100) wafers and Mo sheets for the composition, structural and properties characterization. All substrates were ultrasonically cleaned in an ethanol bath, washed in deionized water, dried in hot air, and then loaded into the PIIP chamber.

Preparation of FB-DLC films was carried out using a pulsed glow discharge mode in the PIIP process where the plasma was generated from a mixture of $B_2H_6 + C_2H_2 + C_2F_6$ deposition gases. The PIIP system that was used has been described in detail elsewhere [8]. The initial pressure in the PIIP deposition chamber was about 10^{-4} Pa. Prior to film deposition, the substrates were sputter cleaned by Ar plasma using the procedure and the parameters reported previously [4]. The deposition of FB-DLC film was carried out by applying a -4 kV pulsed bias voltage to different substrates at a 4 kHz pulse frequency and a 30 μs pulse length, so that an average power density on the surfaces of the growing films was kept about 0.1 W cm^{-2} between the pulses. FB-DLC films with different compositions were deposited by controlling the volume ratio of the feeding gases of $C_2F_6:C_2H_2:B_2H_6$ in the deposition. The volume-per cent ratio of the gases used in the experiments was 14.3:57.1:28.6, 20:60:20, 29.4:47.1:23.5, 29.4:35.3:35.3, 40:40:20, and 50:25:25, respectively. The gas pressure was kept at about 1.33 Pa in all FB-DLC depositions. For comparison, B-alloyed DLC (B-DLC) film was prepared using a low substrate bias of -150 V and a radio-frequency plasma immersion ion process [6], while unalloyed DLC and F-alloyed DLC (F-DLC) films were synthesized using a pulsed glow discharge PIIP process [4]. During the depositions, the sample holder was water cooled to room temperature and a residual gas analyser was used to monitor the plasma component.

The film thickness was measured using a DEKTAK II profilometer. The DLC films were prepared on Si(100) and glass with a thickness of 180–320 nm, and on PMMA and PolyC with a thickness of 250–350 nm. Rutherford backscattering spectrometry (RBS) at 2.4 MeV $^4\text{He}^+$ was used to detect fluorine (F), and resonant ion backscattering spectrometry (RIBS) at 6.66 MeV $^4\text{He}^{2+}$ was used to detect carbon (C) and boron (B) [9, 10]. The hydrogen (H) was measured using the elastic recoil detection (ERD) technique at 2.0 MeV $^4\text{He}^+$ with a 75° incident beam. The chemical concentrations of these elements in the films were calculated from the RBS, ERD and RIBS spectra using the Rutherford Universal Manipulation Program (RUMP), and the accuracy of the elemental contents obtained was within an error range of $\pm 10\%$ [9–11]. The densities of the FB-DLC films were then calculated from the film composition and the film thickness with an uncertainty of $\pm 10\%$.

The Fourier transform infrared spectroscopy (FTIR) spectra were collected from the F-DLC, B-DLC and FB-DLC films deposited on Si(100) by a BIO-RAD FTS-40 Digilab Division Fourier transform infrared spectrometer that was operated in a range of $600\text{--}2400\text{ cm}^{-1}$ and at a resolution of 2 cm^{-1} . The Raman spectra were measured from unalloyed DLC, B-DLC and FB-DLC films deposited on glass with a Renishaw Raman System 2000 imaging microscope that worked with a 20 mW HeNe (514.5 nm) laser and a spectral resolution of 1 cm^{-1} . The Raman spectra were fitted with Gaussian line shapes and the background was subtracted in the simulation. All fitting parameters (the height, width, position, integrated area, etc) were recorded to characterize the bonding features of carbon or carbon with fluorine and boron atoms in the DLC films. The optical transparency and absorption of the FB-DLC coated PMMA and PolyC was measured in the visible light range of $350\text{--}800\text{ nm}$ with an UV/vis (Varian Cary-1C) spectrometer. The optical band gap was determined by fitting the absorption data to a Tauc relation, using the same method as described in [2, 4].

The experimental methods used for measuring the nano-hardness and the water wetting contact angle of FB-DLC films deposited on PMMA, PolyC, glass, and silicon (100) are the same as those used in our previous work [4, 6]. In order to make a comparison, hardness and wetting contact angles were also measured from PTFE (Teflon®), PMMA, PolyC, DLC and B-DLC films. Tribological tests of FB-DLC films were carried out on a pin-on-disc tribometer at room temperature and in air at 15% relative humidity (RH). A smooth, 6 mm diameter ruby ($\text{Al}_2\text{O}_3\text{:Cr}$) ball served as the pin for the FB-DLC coated Si(100). As PMMA and PolyC are soft polymers, a high density polyethylene (HDPE) 6 mm diameter ball was used. The wear track was 3 mm in diameter and the pin sliding speed was 1.9 cm s^{-1} (120 rpm). The wearing tests were carried out by applying a wear load of 1.53 N (equal to an initial Hertzian contact stress of 0.96 GPa) on FB-DLC films and with a maximum of 15 700 wear cycles for FB-DLC on Si(100) and a maximum of 7500 wear cycles for FB-DLC on PolyC and PMMA. The friction coefficient, electronically monitored and recorded in the wearing tests, was averaged from the recorded data with a small fluctuation of $\pm 0.5\%$.

3. Results and analysis

3.1. Composition and bonding structure

Figures 1(a) and (b) show the RIBS and RBS spectra, which characterize the existence of C, F, and B in the 5.6 at.% B and 12.9 at.% F alloyed DLC film. The DLC coated Mo sheet was used in the RIBS measurement as the small amount of B alloying could be clearly identified by a collected small peak on the spectra. There is no detectable oxygen in either the RIBS or RBS spectra, indicating that the oxygen contamination in the DLC films is negligible. An ERD spectrum, presented as an inset plot in figure 1(a), shows a small amount of H incorporated

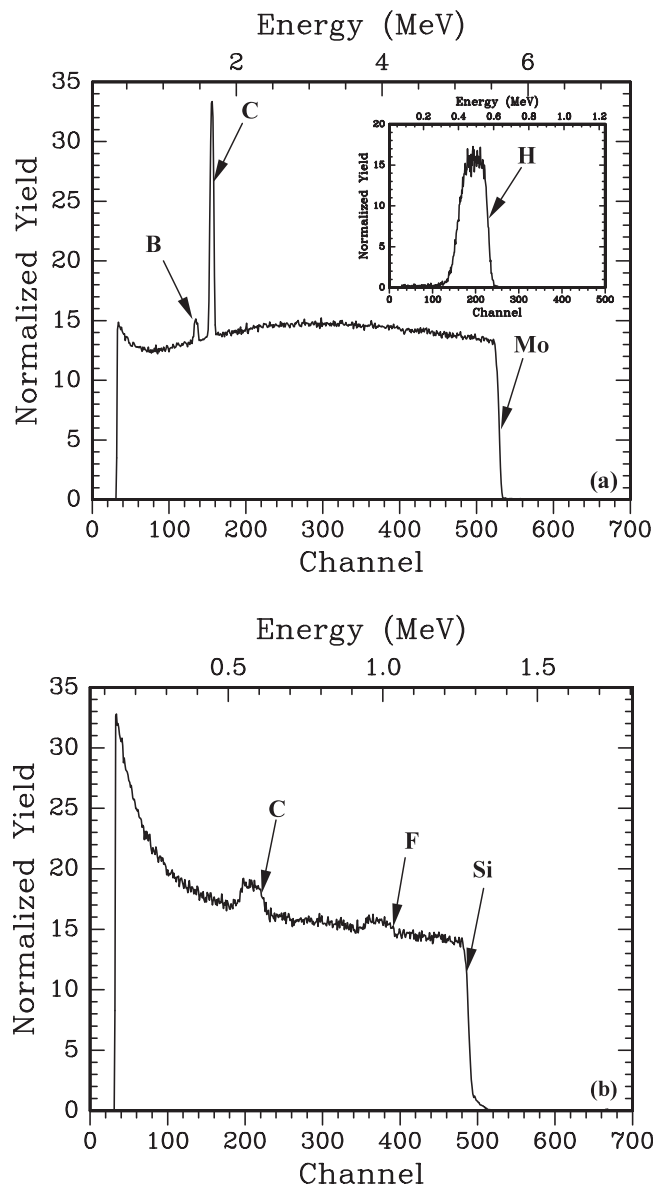


Figure 1. (a) IRBS spectrum of the FB-DLC film on Mo and (b) RBS spectrum of the FB-DLC film on Si(100). The plot in the inset in (a) is an ERD spectrum obtained from the film for hydrogen content measurement. The beam-incidence angle was 75° for ERD measurements.

in the FB-DLC film, as compared with what has been observed in B-alloyed DLC films [6]. The chemical composition of all FB-DLC films was measured and calculated. The results indicated that while the FB-DLC film is alloyed with B with a concentration level of about 4–6 at.%, the increase of F alloying, from 0 to 17.7 at.%, corresponds to a monotonic decrease of H incorporation, from 30.5 to 7.1 at.% in the deposited films [7].

The atomic bonding configuration in the DLC films was characterized by FTIR spectroscopy. Figure 2 shows the IR spectra of the B-DLC, F-DLC, and FB-DLC films

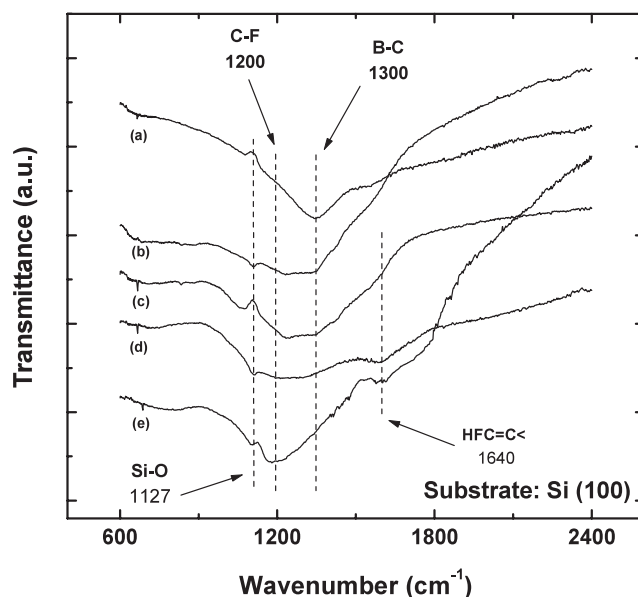


Figure 2. IR spectra of B-DLC, F-DLC, and FB-DLC films. The film compositions: (a) 4 at.% B, 28 at.% H; (b) 6.2 at.% F, 3.8 at.% B, 22.1 at.% H; (c) 10.5 at.% F, 4.2 at.% B, 18.4 at.% H; (d) 17.7 at.% F, 4.5 at.% B, 7.1 at.% H; and (e) 19.7 at.% F, 3.1 at.% H. The films were deposited on Si(100) with a thickness of 180–320 nm.

in different chemical compositions. The main absorption bands at wavenumbers of about 1300 cm^{-1} (spectrum (a)) and about 1200 cm^{-1} (spectrum (e)) can be identified as the C–B stretch vibration bonding in the B-DLC film [12, 13], and as the C–F vibration modes in the F-DLC film [3, 5], respectively. For the DLC films co-alloyed with B and F, the series of IR spectra (b)–(d) shows a main absorption band in a wavenumber range of $1200\text{--}1360\text{ cm}^{-1}$. This peak is clearly a composite band resulting from the superpositioning of the C–B stretch modes at 1200 cm^{-1} and the C–F vibration modes at 1300 cm^{-1} . There is another absorption peak at around 1640 cm^{-1} , which reflects the HFC=C< vibrating band [5]. The IR data suggest that the C–C bonding structure is hybridized with C–F and C–B bonds in the FB-DLC films. In particular, figure 2 shows that for a nearly fixed B content of 3.8–4.5 at.%, an increase in F concentration from 6.2 to 17.7 at.% (spectra (b)–(d)) results in a broadening of the main absorption band at $1200\text{--}1360\text{ cm}^{-1}$ and an increase in the intensity of the absorption peak at about 1640 cm^{-1} , which is indicative of an increase in the number of C–F bonds in the FB-DLC films [5]. A very weak peak around 1127 cm^{-1} indicates the presence of a negligible amount of Si–O bonds existing at the interface between the film and the Si(100) substrate, as no O signal was detected from the films deposited on the Mo substrate by IRBS (see figure 1).

Figure 3 shows the Raman spectra measured from the unalloyed, FB-alloyed, and B-alloyed DLC films which were all prepared on the glass substrate. It can be seen that all Raman spectra show the amorphous bonding features of the DLC film [2], even the DLC films that were alloyed with B or B and F, respectively. The inset plot is a Raman spectrum decomposed into bands with Gaussian line shapes, in which the fitted line agrees well with the experimental data. The Raman spectra show that all DLC films consist of a relatively broad peak at around 1550 cm^{-1} and a shoulder at around 1345 cm^{-1} , commonly referred to as the G band and D band, respectively [14]. The D and G peaks both originate from the sp^2 bonded part in amorphous carbon films; the G-peak position is microscopically correlated with

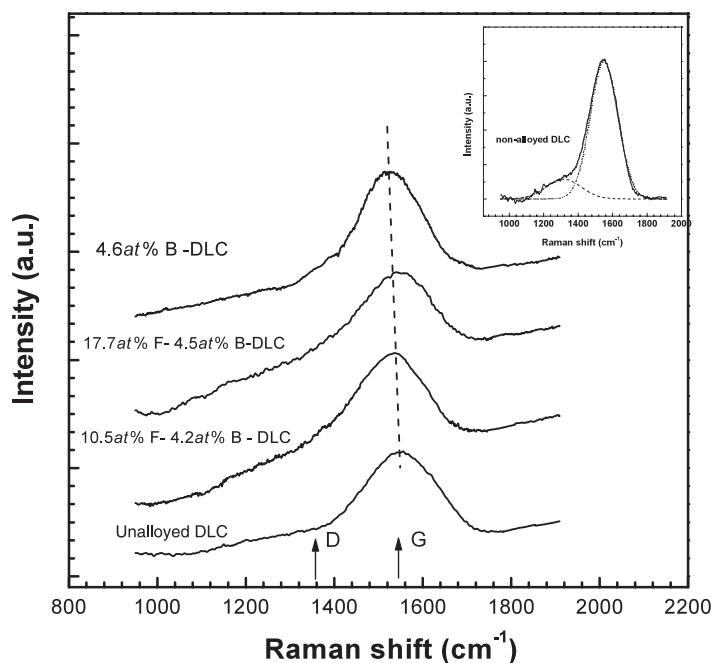


Figure 3. Raman spectra of unalloyed, FB-alloyed, and B-alloyed DLC films prepared on glass by PIIP deposition. The plot in the inset is an example of a Raman spectrum decomposed into the G and D bands with Gaussian line shapes.

the bond strength and angle, and the microstructure of the film [14, 15]. The G and D peak positions, G-peak FWHM (full width at half maximum), and relative intensity of the D and G peaks (I_D/I_G) as a function of the chemical composition of the films are shown in figures 4(a) and (b), respectively. On associating the data measured from the DLC films with those from B-DLC films, as shown in figure 4(a), it can be seen that alloying B into DLC films induces both G and D peak positions simultaneously to shift to lower Raman frequency, which is an indication of the enhancement of sp^3 fourfold coordinate bonding in the amorphous carbon films [15]. In addition, figure 4(b) shows that B-alloyed DLC film has an increase of G-band width and a decrease of the intensity ratio of the D and G peaks (I_D/I_G), respectively. The increase of the G-band width is correlated with increasing mass density and hardness of the DLC films, as indicated by Tamor and Vassel [14]. The I_D/I_G ratio originally varies inversely with the size of the graphite crystallites, i.e., $I_D/I_G = k/L_a$, where L_a is the sp^2 correlation length or in-plane crystallite size. When the regime L_a is smaller than 12 Å, a lower I_D/I_G ratio means smaller sp^2 cluster size [16]. The increase of G-band width with the concurrent decrease of I_D/I_G , as well as the simultaneous downshift in both the G and D peaks, as shown in figures 4(a) and (b), could suggest that incorporation of around 5% B into DLC films promotes the formation of a film with an enhanced sp^3 bonding structure [6].

However, the co-alloying of B and F into DLC films shows a complicated interaction on the bonding structure of the DLC films. The data in figure 4(a) show that the co-alloying of B to about 4.5 at.% and F up to 10.5 at.% into the DLC films results in the movements of the D peak to high Raman frequency, which may suggest the formation of more graphite-like sp^2 -bonded carbons, but the simultaneous downshift of the G band may suggest, on the other hand, the reduction of the sp^2 -bonded carbons [3, 6]. It can be seen that while the B is about

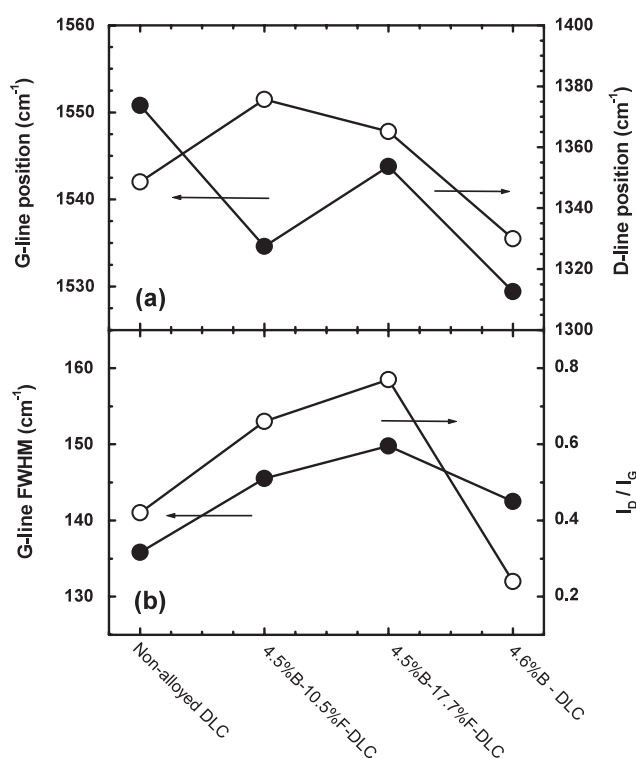


Figure 4. (a) G-peak and D-peak positions and (b) G-peak FWHM and relative intensity ratio of the D and G peaks (I_D/I_G) as a function of the chemical composition of the DLC films.

4–6 at.% in the films, further increase of F content from 10.5 to 17.7 at.% induces both G and D peaks to move to high frequencies, which indicates the increase of the sp^2 bonding fraction in the DLC films. In addition, as compared with unalloyed DLC films, the data in figure 4(b) show that the alloying of F into the DLC films widens the G band but also simultaneously raises the intensity ratio of the D and G peaks (I_D/I_G). The increment in the D-band width is higher than that in the G-band width, and the intensity ratio I_D/I_G reaches a high value at the F concentration of 17.7 at.%. The increase in the intensity ratio of the D and G peaks (I_D/I_G) may result in an increase of the sp^2 bonding but a decrease of the sp^2 cluster size [16], while the increase of the G peak width may reinforce the density and hardness of the DLC films [14]. It could be understood that the incorporation of B promotes the formation of diamond-like sp^3 -bonded carbons [6], and the increase of F alloying could reduce the size of sp^2 -bonded clusters. However, alloying of F to 17.7 at.% or higher will definitely increase the sp^2 bonding fraction in the DLC films. This is because the coordination number of C is four and that of F is one; the formation of F–C bonds corresponds to the creation of C–C bond terminations. The increase of F–C hybridization is correlated with the decrease of the amount of C–C cross linking and the increase of sp^2 bonding in the DLC films [3].

3.2. Physical and mechanical properties

Figures 5(a) and (b) show that the wetting contact angle, H concentration and optical band gap of the FB-DLC films all vary as a function of F concentration, while the B alloying was

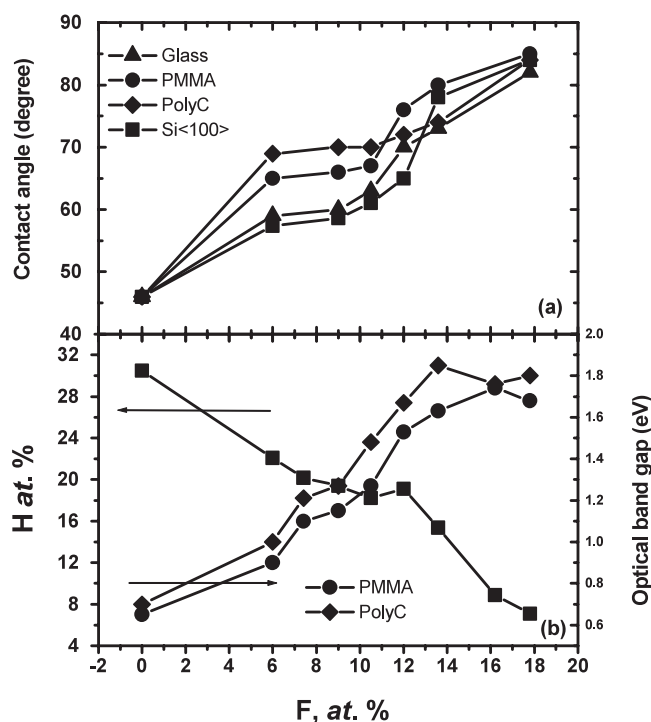


Figure 5. (a) Wetting contact angle and (b) H concentration and optical band gap of FB-DLC films. FB-DLC films prepared on Si(100) and glass have a thickness of 180–320 nm. FB-DLC films deposited on PMMA and PolyC have a thickness of 250–350 nm.

held nearly constant at 4.0–6.0 at.% in the films. Clearly, the data in figure 5(a) show that the wetting contact angle for water on FB-DLC films increases with increasing F concentration for substrate types, indicating improvement on the hydrophobic performance of the DLC films with F incorporation. It can be seen that when the F alloying is about 6.2–10.5 at.%, as the data show in figure 5(a), the contact angles vary obviously with changes of the substrates in the order Si(100), glass, PMMA and PolyC. However, the fluctuation on the wetting contact angles monotonically decreases on increasing the F alloying, and almost vanishes when the F content reaches 17.7 at.% in the FB-DLC films. The results show that the DLC film alloyed with 17.7 at.% F and 4.5 at.% B is the most hydrophobic, with contact angles of 82°–84°. These contact angles are much closer to our measured value of 88° for PTFE (Teflon®) and are much higher than that of PMMA (42°), PolyC (40°), or unalloyed DLC (46°).

The interrelationship between F concentration, H concentration and the optical band gap of FB-DLC films, as presented on figure 5(b), indicates that the F and H concentrations are inversely correlated with the band gap that increases with increasing F concentration and decreasing H concentration. The largest optical band gap (1.68–1.82 eV) occurs for the lowest H concentration (7.1 at.%). This trend, as shown by the data in figure 5(b), differs considerably from what has been normally observed in a-C:H DLC films, where the optical properties are improved with increasing hydrogen incorporation [1, 2]. As the B concentration has been kept nearly constant (4.0–6.0 at.%), the increase in the optical gap energy with F concentration is believed to be attributed to the high C–F bonding hybridization in FB-DLC films (see figure 2) as the strength of the bond between C and F atoms is larger than that of the bond between carbon atoms [5].

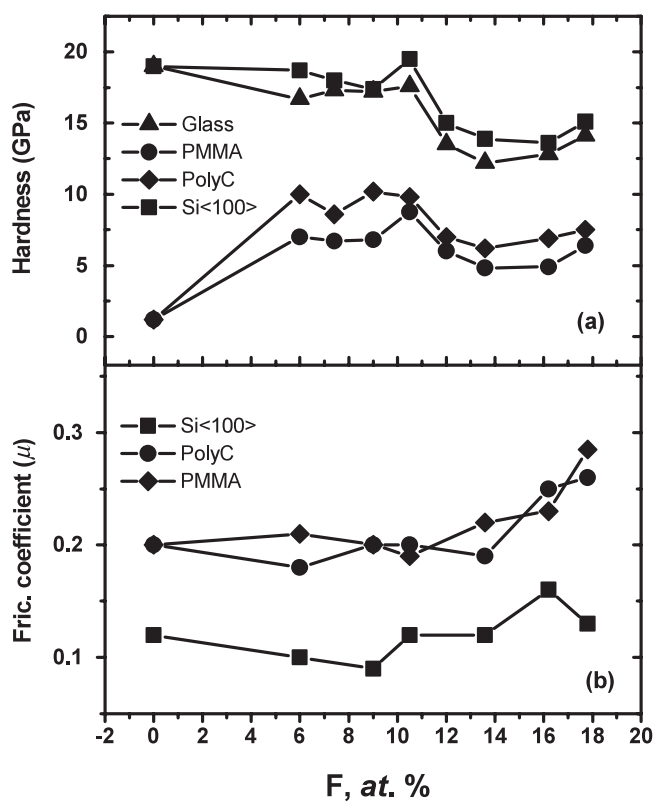


Figure 6. (a) Hardness and (b) friction coefficients of the FB-DLC films. FB-DLC films prepared on Si(100) and glass have a thickness of 180–320 nm. FB-DLC films deposited on PMMA and PolyC have a thickness of 250–350 nm.

The influences of F and B co-alloying on the hardness and friction coefficients of the DLC films are illustrated in figures 6(a) and (b). First, the data in figure 6(a) show that the hardness of FB-DLC is sensitive to both substrate type and F concentration. Since the FB-DLC films are relatively thin (≤ 350 nm) and PMMA and PolyC are soft polymers, our hardness measurements are a composite measure of the coating and the substrate hardness. While the absolute values of the hardness can differ significantly, the relative changes and trends observed as a function of F concentration are very similar. Most significantly, these data show that the addition of an approximately 300 nm thick FB-DLC film ($F = 6.2$ at.% and $B = 3.8$ at.%) to the softer substrates, PMMA and PolyC, results in a hardness of 7 and 10 GPa, respectively. The hardness of FB-DLC coated plastic samples is significantly higher not only than that of uncoated PMMA (0.4 GPa), PolyC (0.3 GPa), and PTFE (Teflon®) (0.8 GPa), but also than that of the unalloyed DLC coated PMMA (1.2 GPa). The addition of FB-DLC to Si(100) and glass results in a hardness of about 18–20 GPa, nearly unchanged relative to the unalloyed DLC case. An increase in F alloying up to 10.5 at.% has little effect on the hardness, independent of substrate. Additional increases in F concentration soften the FB-DLC films; at the maximum F concentration of 17.7 at.% the hardness of FB-DLC coated Si(100) and glass is decreased to 14–15.2 GPa while the hardness of FB-DLC coated PMMA and PolyC is decreased to 6.5–7.7 GPa.

The friction and wear performances are closely correlated with variation of the hardness of the DLC films. As the B alloying is about 4.0–6.0 at.% in the films, the increase of the F

concentration up to 10.5 at.% has no obvious influence on the hardness of FB-DLC films (see figure 6(a)). As a result, the friction coefficients measured from the FB-DLC films are almost the same as those of unalloyed DLC films, around 0.11 for DLC films on Si(100), and around 0.2 for DLC films on both PMMA and PolyC. However, further increase of the F alloying, up to 17.7 at.%, resulted in a reduction of the hardness and thus an increase of the friction coefficient, from 0.12 to 0.16 for DLC films on Si(100), and from 0.22 to 0.28 for DLC films on PMMA and PolyC (see figure 6(b)). Since the wear coefficients are about 0.4–0.45 for an HDPE ball sliding on PMMA and PolyC, it can be confirmed that the FB-DLC coated polymers, PMMA and PolyC, have the enhanced wear-resistant performance. Even the PMMA coated with a FB-DLC film with a maximum of 17.7 at.% F still has a friction coefficient of 0.28, at least 30% less than that of the PMMA. In addition, it is clear that the friction coefficient of DLC films on Si(100) is much lower than those of DLC films on both PMMA and PolyC. An original high surface roughness of polymers (i.e. PMMA is about 8.5 nm), much higher than that of Si(100) (about 0.32 nm), could be correlated with higher friction coefficients [17].

4. Discussion

In PIIP depositions, the DLC films are synthesized under ion bombardment that is induced by a pulsed bias, -4 kV, applied on the substrates [8]. The energetic ion bombardment on the growing films could affect the formation of the FB-DLC films with different composition and structure [9]. Compared with Si(100), glass, PMMA and PolyC are poor conductive materials. When the PIIP depositions are carried out on glass, PMMA and PolyC, the applied bias may drop down on the substrate surfaces, which weakens the ion bombardment on the growing films and results in changes in composition and structure of the DLC films. On the other hand, the H incorporation could induce the formation of a polymer structure in the amorphous carbon films [1, 2], which further enhances the insulation of the substrates. Therefore, the wetting contact angles of water on FB-DLC films fluctuate obviously when the films are deposited on different substrates with an F alloying below 10.5 at.% but H incorporation above 18 at.%, as the data in figures 5(a) and (b) show. It is expected that the increase of F alloying, realized by inputting more C_2F_6 in the PIIP DLC deposition, suppresses the H incorporation and results in an increase of sp^2 carbon bonds in the FB-DLC films, which could enhance the conductivity of the growing films and lead to the formation of DLC films, under the ion bombardment, with a similar composition and bonding structure on the different substrates. The data in figures 5(a) and (b) clearly indicate that the fluctuation of the wetting contact angles is monotonically declining with increasing F alloying and simultaneous decreasing H content in the FB-DLC films, and is even down to zero when the F alloying is up to 17.7 at.% and H content down to 7.1 at.%. The experimental results in this study show that the F alloying enhances the energetic ion bombardment and promotes the PIIP deposition of DLC films on different substrates with the same properties, as the FB-DLC film alloyed with F above 10.5 at.% exhibits the similar hydrophobic performance for different substrate types.

The increase of F alloying results in an increase of F–C hybridized bonds (see figure 2) and the reduction of H incorporation (see figure 5(b)), which changes the bonding structure and affects other properties of the DLC films. As compared with unalloyed DLC films and B-alloyed DLC films, the incorporation of F induces the increase of both the G peak width and the intensity ratio I_D/I_G of the D and G peaks, which is an indication of the reduction of the size of the sp^2 bonding clusters in the DLC films and benefits the improvement on the film properties, such as the density and hardness. On the other hand, the alloying of F into DLC films induces the formation of F–C bonding and increases the sp^2 C–C bonding fraction in the films, which results in a reduction of the density and hardness but an increase of the optical gap. The purpose

Table 1. Composition and properties of DLC and alloyed DLC films on PMMA. (Note: θ and E_{obg} are the contact angle against water and the optical band gap, respectively. The films deposited on PMMA have a thickness of about 300 nm.)

Material	F (at.%)	B (at.%)	H (at.%)	Density (g cm ⁻³)	θ (deg)	E_{obg} (eV)	Hardness (GPa)	Friction coeff. (μ)
DLC	0	0	30.5	2.8	46	0.8	1.2	0.22
B-DLC	0	4	28	2.2	51	2.1	5.7	0.21
F-DLC	19.7	0	3.1	2.2	85	1.6	1.0	0.32
FB-DLC	17.7	4.5	7.1	2.2	83	1.8	6.5	0.28
PTFE (Teflon®)	67	0	—	—	88	—	0.8	—

of alloying B into the DLC films is to increase the sp^3 C–C bonds and to compensate for the loss of properties, as it was found that the DLC films alloyed with 4–6 at.% B could have an enhanced hardness up to 26.7 GPa [6]. The experimental results in this study show that when the F concentration is increased up to 10.5 at.%, the induced increase in sp^2 C–C bonding can be compensated by the reduction of the size of the sp^2 bonding clusters induced by F alloying and the increase of the sp^3 bonding induced by B alloying. As a result, the DLC films alloyed with 4.0–6.0 at.% B and 6.2–10.5 at.% F exhibit high density, high hardness, improved hydrophobic and tribological properties, as the data show in figures 5 and 6 and in published work [7]. A further increase of F incorporation from 10.5 to 17.7 at.% induces the obvious increases of F–C bonds and sp^2 C–C bonds in the FB-DLC films, as deduced from figures 2 to 4, whose influence overwhelms the benefits produced by the B alloying and leads to the formation of an FB-DLC film with low hardness (down to 6.5 GPa for PMMA and PolyC, and to 14–15.2 GPa for Si and Glass), and high friction coefficient (up to 0.28), as the data show in figures 5 and 6. However, the increase of the F–C bonding hybridization further enhances the hydrophobic and optical performance (wetting contact angle up to 82°–84° and optical gap up to 1.8 eV) and decreases the H incorporation (down to 7.1 at.%).

Table 1 indicates the compositions and properties of DLC and alloyed DLC films deposited on PMMA substrate. For comparison, the properties of PTFE (Teflon®) are added in table 1. It can be seen that B-alloyed DLC film has high hardness of 5.7 GPa, high optical gap energy 2.1 eV and low friction of 0.21; however, the contact angle of B-DLC to water (51°) is very close to that of unalloyed DLC films (46°). On the other hand, F-DLC film incorporated with 19.7 at.% F has a contact angle of 85° that is almost the same as PTFE (Teflon®) (88°), but a relative low hardness of 1 GPa and high friction coefficient of 0.32. The hardness of F-DLC films is almost the same as that of the unalloyed DLC films; the low hardness may result from high H concentration in unalloyed DLC films and high F concentration in F-DLC films. Comparatively, the DLC films alloyed with 17.7 at.% F and 4.5 at.% B show an optimal balance of large contact angle of 83°, increased hardness of 6.5 GPa, high optical band gap of 1.8 eV, and a friction coefficient of 0.28 that is lower than that of F-DLC films. In particular, FB-DLC film formed on PMMA and PolyC has a high hardness and optical gap energy, while its H concentration (7.1 at.%), comparable to that in F-DLC (3.1 at.%), is much lower than that in both DLC and B-alloyed DLC films (see the data in table 1). It can be confirmed from the above analysis that the increased hardness and the enhancements of the hydrophobic, optical and tribological performances are benefits from the reduction of H concentration and the formation of B–C and F–C hybridized bonds in the PIIP deposited FB-DLC films [4, 6].

5. Conclusion

F and B co-alloying could enhance the PIIP deposition of DLC films on different substrate materials with improved hydrophobic and optical properties. Because of the incorporation of

F–C and B–C hybridization into the DLC structures, the PIIP synthesized FB-DLC films on optically transparent glass and polymers possess many positive properties observed in F-DLC and B-DLC films. The results indicated that by maintaining the B alloying in a concentration level of 4.0–6.0 at.% and varying the F alloying in concentrations between 6.0 and 17.7 at.%, FB-DLC films with low hydrogen incorporation, enhanced hardness and reduced friction coefficients, increased wetting contact angle, and high optical band gap can be obtained. In fact, the DLC films can be FB-alloyed to be as hydrophobic as PTFE (Teflon®) (wetting contact angles of $\sim 84^\circ$) while maintaining an optical gap (1.8 eV), low friction coefficient (< 0.28), and a high hardness that exceeds PMMA by a factor of 18, polycarbonate by a factor of 23, and PTFE (Teflon®) by a factor of 9. The property enhancements are attributed to the reduction of H incorporation and the formation of F–C and B–C hybridization in the PIIP synthesized FB-DLC films. The fact that these coatings have been made by PIIP deposition indicates that FB-DLC films can be applied to large and complex shaped optical materials through PIIP.

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