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# Soft X-ray irradiation effect on the fluorinated DLC film

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## ABSTRACT

The irradiation effect on fluorinated diamond-like carbon (F-DLC) film was investigated by measuring the dose dependence of various film properties using synchrotron radiation (SR) in the soft X-rays in the SR dose region from 0 to 2000 mA h. Film flatness was maintained but various film properties and surface properties were found to be changed by the SR irradiation. Wettability of the F-DLC film surface increased dramatically within 20 mA h SR exposure, which was ascribed to the decrease in fluorine on the film surface. Film thickness, film density, composition ratio of fluorine atom in film decreased and $sp^2$ / ($sp^2$ + $sp^3$) ratio of carbon atoms increased within 300 mA h SR exposure, which were ascribed to the desorption of species containing fluorine atoms. In addition, dominant desorbed species emitted from F-DLC film were found in the fluorocarbon group, $CF_x$. Changes in film properties and film thickness did not proceed, when fluorine content in the F-DLC film decreased to about 10% after the 300 mA h SR exposure.

## 1. Introduction

Diamond-like carbon (DLC) film is an amorphous material that consists of $sp^2$ hybridized carbon equivalent to the graphite structure, $sp^3$ hybridized carbon equivalent to the diamond structure and hydrogen. DLC films have superior properties such as high hardness, low friction coefficient, chemical inertness and gas barrier, and are used widely as coating materials in various industrial fields [1–3].

It is well known that DLC films that contain other elements show various functionalities. For instance, those that contain titanium show burning resistance [4–6], and those that contain silicon show high resistance to oxidation [4,7]. It was reported that fluorinated DLC (F-DLC) films showed particularly high insulation, low-dielectric constant, surface smoothness, low surface free energy and chemical inertness [8–12]. Judging from these properties, we expected that F-DLC films can be utilized as antifouling coatings, insulators or low-*k* materials in electronic devices and anticorrosion coatings [13,14]. In semiconductor processing, the light source will shift from ultraviolet rays to soft X-rays due to the further high integration and miniaturization that will be achieved for integrated circuits in the near future. Moreover, with the development of aerospace, the materials used in outer space will confront the problem of material corrosion by atomic oxygen and material modification incurred with soft X-ray irradiation. Thus, the smooth insulation films and anticorrosion coatings which are available under the soft X-ray irradiation will be required in various industrial fields. In general, DLC films have very strong tolerance for soft X-ray irradiation [15]. However, it was recently reported that the soft X-ray irradiation on H-DLC films or DLC films containing other elements can decrease film thickness and deteriorate film properties [16–18]. Therefore, it is necessary to understand the effects soft X-rays have on F-DLC films, before such films are put into practical use through the use of soft X-ray irradiation.

In this study, we wished to investigate the irradiation effect of soft X-rays on the surface of F-DLC films. To achieve this, we measured the SR dose dependence on film thickness, elementary composition ratio, carbon and fluorine chemical bonding states, and the local structure of the carbon and $sp^2$ / ($sp^2$ + $sp^3$) ratio of carbon of F-DLC films. We also examined and discussed the process of modifying F-DLC films by using soft X-ray irradiation.

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## 2. Experimental methods

We performed soft X-ray irradiation on F-DLC films at BL06 in the NewSUBARU synchrotron facility of the University of Hyogo [19]. The experimental apparatuses at BL06 have been described in detail in previous reports [20,21]. The SR extracted from a bending magnet, which is the light source of BL06, was introduced to the sample stage as a straight beam via a pair of mirrors. The SR at the BL06 sample stage had a continuous spectrum from infrared to soft X-rays, below 1 keV. Calculated photon flux is almost constant from 30 eV to 1000 eV. This energy range includes 300 eV and 690 eV, which are the ionization energy of a carbon *K* shell and a fluorine *K* shell. In this experimental condition, reactions on the surface of F-DLC film were considered to be dominantly caused by soft X-rays, but UV photons were also included. During this experiment, the electron energy of the NewSUBARU ring was 1.0 GeV and the ring current was 300 mA in the top-up mode. The SR was irradiated onto the film surface perpendicularly, except for the detection of desorbed species using a quadrupole mass spectrometer. The SR dose [mA h] was derived from the product of the ring current [mA] and exposure time [h]. During the time the F-DLC film was being exposed to SR, the pressure in the irradiation chamber was on the order of $10^{-5}$ Pa and the sample stage temperature was confirmed to be room temperature using a thermocouple. After SR exposure, the modified F-DLC film was kept in a dry box.

Fluorinated DLC film was deposited on Si wafers using an amplitude-modulated radio-frequency plasma-enhanced chemical vapor deposition method (Nippon ITF Co.) [22]. The desired film thickness was 200 nm. The as-deposited F-DLC film was light green and with SR exposure it changed to deep blackish green.

## 3. Results and discussion

To investigate the process through which soft X-ray irradiation modified F-DLC films' surfaces, we exposed such films to synchrotron radiation (SR) in the soft X ray region in the dose region from 0 to 2000 mA h and measured the degree to which the films' properties depended on the SR dose dependence. We used an atomic force microscope (AFM) to observe the films' surface shape and X-ray reflection (XRR) measurements to estimate the films' density. To measure the film thickness, we used a scanning electron microscope (SEM) to observe section images. To measure the step depth created by the SR irradiation we used a stylus profiler and XRR. We used X-ray photoelectron spectroscopy (XPS) and a combination of elastic recoil detection analysis (ERDA) and Rutherford backscattering spectrometry (RBS) to measure the elemental composition on F-DLC film surfaces and that in the films themselves. We examined the chemical state and local structure of carbon atoms by using the C 1*s* XPS spectrum and the C *K*-edge near-edge X-ray absorption fine structure (NEXAFS) spectrum, respectively. We used the contact angle of a water drop against the F-DLC film surface obtained with a contact angle meter to measure film surface wettability. To measure species desorbed from the F-DLC film surface, we used a quadruple mass spectrometer that irradiated the ions with soft X-rays.

### 3.1. Film thickness by X-ray reflection, scanning electron microscope, and stylus profiler

To estimate the degree to which F-DLC film thickness depended on the SR dose, we observed F-DLC film section images, measured step depths created by SR irradiation, and took XRR measurements. We obtained the F-DLC film section images by using an SEM (JEOL JSM-6700F) to observe F-DLC films divided with substrate Si wafer. For taking step depth measurements, the F-DLC films were exposed to SR through an Au mesh (wire diameter φ 0.07 mm, 100 mesh/in) as a mask. The step depth was estimated by using a stylus profiler (DEKTAK 6 M) to measure the difference in altitude between the area exposed to SR and a shadow area due to the Au mesh. Film thicknesses were obtained by subtracting the step depth with stylus profiler from the film thickness of the F-DLC film, 216 nm, before the SR exposure measured by the SEM. We used an XRR apparatus (Mac Science, M03XHF MXP3) to take the XRR measurements.

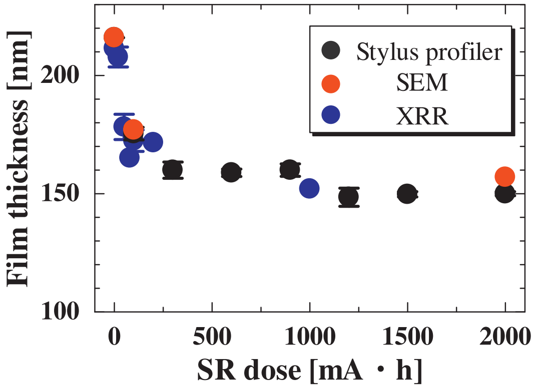


**Fig. 1.** Film thickness dependence on SR dose with Stylus profiler (black circles), SEM (red circles), and XRR (blue circles).

Fig. 1 shows the degree to which the soft X-ray irradiation caused the film thickness to be dependent on the SR dose. The red and blue points respectively show the film thicknesses estimated from SEM and XRR measurements. The black points show film thickness estimated from stylus profiler measurements, before SR exposure measured by SEM, 216 nm. Film thicknesses estimated from stylus profiler measurements accorded well with those estimated from SEM and XRR measurements. The thicknesses decreased substantially to about 170 nm after 50-mA h SR exposure. At doses of more than 50 mA h, the thicknesses gradually decreased and remained constant at 150 nm at doses of 300 mA h or more. From these results, we confirmed that the F-DLC film thicknesses decreased due to soft X-ray irradiation, but that the decrease was stopped at doses of 300 mA h or more. In other words, F-DLC films were not exhausted after surplus SR irradiation.

### 3.2. Surface observation using AFM

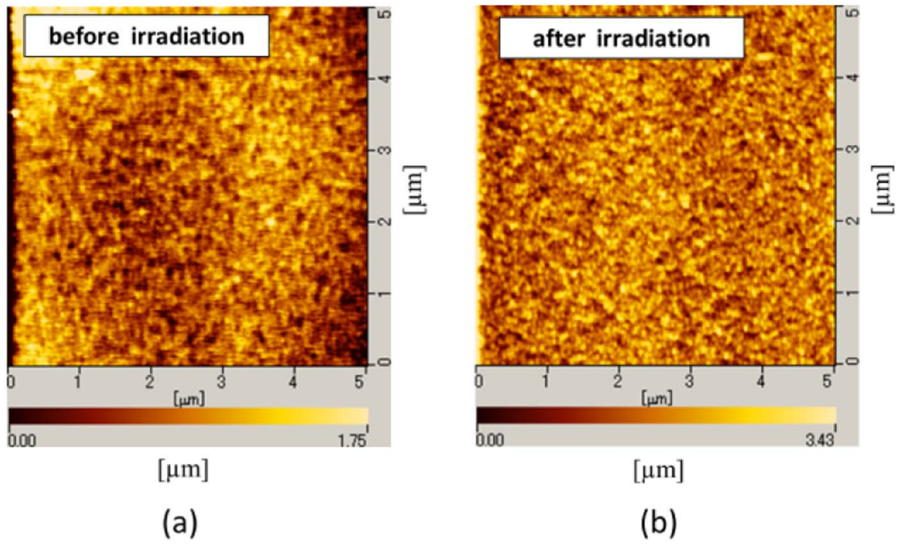
We used AFM to observe the surfaces, which enabled us to compare the surface coarseness of the F-DLC films before and after the soft X-radiation. The AFM we used to observe F-DLC film images was the *E*-sweep/NanoNavi Station product provided by SII Nanotechnology with dynamic force mode. Fig. 2 shows F-DLC film surface images (a) before irradiation and (b) after irradiation with 1000 mA h. No significant changes were not observed between them. The arithmetic average roughness (Ra) values of the film surface were estimated to be 0.288 nm in (a) and 0.404 nm in (b). This was confirmed that the films maintained high flatness after SR exposure.

### 3.3. Film density from X-ray reflection measurements

We carried out XRR measurements to obtain the density of the films. Fig. 3 shows the dependence of the film density on SR dose obtained from XRR measurements. The film density before irradiation was ≈ 2.0 g/cm$^3$, but after 50-mA h SR exposure it markedly decreased to ≈ 1.7 g/cm$^3$. At doses of more than 50 mA h it remained constant at 1.7 g/cm$^3$. From these results, we confirmed that soft X-ray irradiation decreases F-DLC film density.

### 3.4. Elementary F-DLC film composition obtained by combining of elastic recoil detection analysis and Rutherford backscattering spectrometry

We combined ERDA and RBS to estimate the elemental compositions of F-DLC films, using a tandem electrostatic accelerator (National



(a) (b)

**Fig. 2.** Micrograph of F-DLC film surface obtained from AFM. (a) Before irradiation. (b) After irradiation with 1000 mA h.

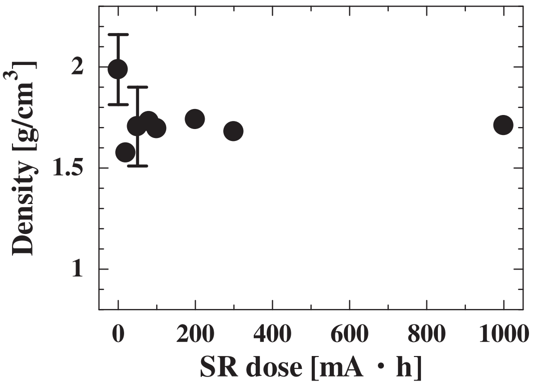


**Fig. 3.** Film density dependence on SR dose, based on XRR measurements.

Electrostatic Corporation, 5SDH) located in the Faculty of Maritime Sciences, Kobe University [23,24]. A sample was irradiated by a 4.2 MeV $He^{2+}$ beam to accelerate the negative helium ions ($^4He^-$) generated by the RF-discharge negative-charge-exchange ion source. The incident angle of the beam was 15° with respect to the sample surfaces. As for the RBS, high-energy $He^{2+}$ ions scattered elastically from the sample, they were captured with a solid-state detector (SSD) positioned at 160° with respect to the beam direction. As for the ERDA, $He^{2+}$ ions collided elastically with hydrogen atoms in the sample. The hydrogen atoms ejected from the sample were detected with an SSD positioned at 30° with respect to the beam direction.

We estimated that the hydrogen content in the as-deposited F-DLC film was less than 2%. We obtained this estimation by comparing the hydrogen signal intensity obtained in the ERDA spectra with the carbon and fluorine intensities obtained in the RBS spectra. It is likely from the above result that the present F-DLC films are almost hydrogen-free, and these atoms may originate from the impurity molecules adsorbed onto the F-DLC samples. In other words, we felt that this film included almost no hydrogen. Fig. 4 shows the dose dependence of the fluorine composition ratio in the F-DLC films. The atomic ratio of fluorine was about 0.5 before the SR irradiation, and it decreased dramatically to 0.3 after 50-mA h SR exposure. At doses of more than 50 mA h, the fluorine ratio gradually decreased and remained constant at 0.25 at doses of more than 300 mA h. From these results, we confirmed that the fluorine ratio in the F-DLC film decreases due to soft X-ray irradiation and that ≈ 25% of fluorine remains in F-DLC films after surplus SR irradiation.

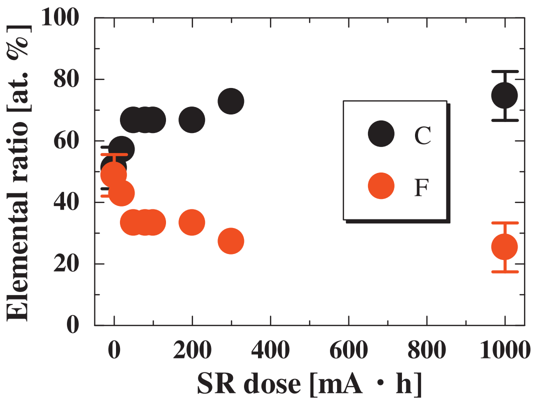


**Fig. 4.** Elemental composition ratio dependence on F-DLC film bulk on SR dose, estimated by combining ERDA and RBS. Black and red circles respectively indicate carbon and fluorine ratio.

### *3.5. Elementary composition and chemical state of F-DLC film surface by X-ray photoelectron spectroscopy*

We estimated elementary composition of the F-DLC film surface by using a conventional X-ray photoelectron spectroscopy (XPS) apparatus (ULVAC-PHI, PHI X-tool). The Mg Kα line (1253.6 eV) was used as the X-ray source. Fig. 5 shows the dose dependence of the atomic composition of the F-DLC film surface. The black and red points respectively

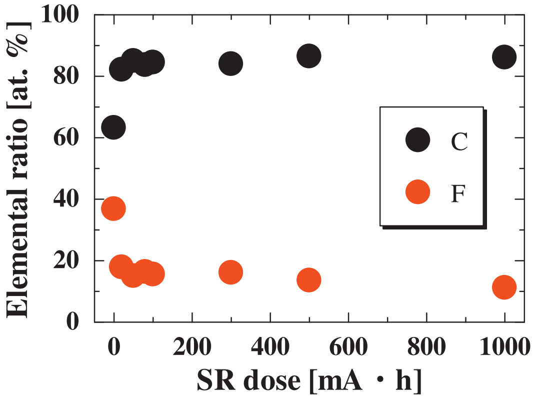


**Fig. 5.** Elemental ratio of F-DLC film surface dependence on SR dose with XPS. Black and red circles respectively indicate carbon and fluorine ratio.

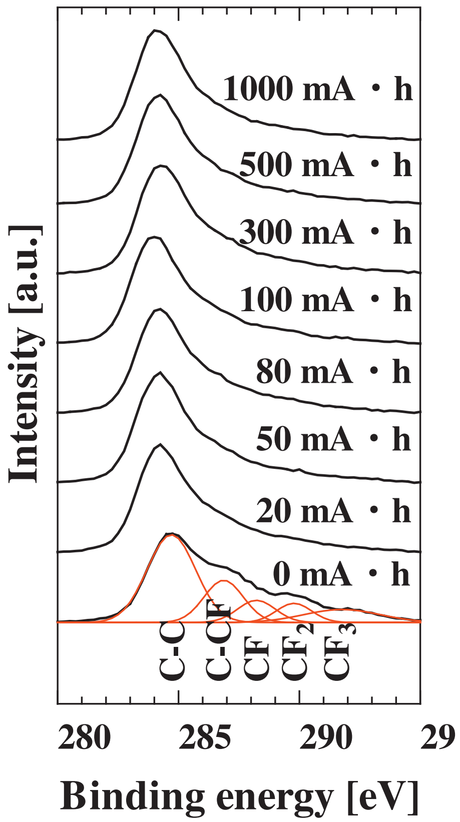


**Fig. 6.** Dependence of C 1*s* XPS spectrum of F-DLC film on SR dose.

show carbon and fluorine contents. The fluorine and carbon contents in the F-DLC film surface before irradiation were ≈ 0.4 and ≈ 0.6, respectively. The fluorine content substantially decreased to ≈ 0.2 after 20 mA h SR exposure. At doses of more than 20 mA h, the fluorine ratio gradually decreased but remained at ≈ 0.1 at a 1000 mA h dose.

The dependence of the C 1*s* spectra on F-DLC films on SR dose is shown in Fig. 6. The C peak of the F-DLC film before irradiation can be decomposed into five sub-peaks, which are centered at 284.70 eV (—C—C), 286.87 eV (—C—CF), 288.22 eV (—CF), 289.78 eV (—$CF_2$) and 291.76 eV (—$CF_3$) [25–28]. It is clear from the figure that the peak intensities are derived from increased —C—C and that those derived from —C—CF, —CF, —$CF_2$ and —$CF_3$ decreased as the SR dose increased in the 0–50 mA h SR dose range. The —$CF_2$ and —$CF_3$ peaks almost disappeared after 50 mA h SR exposure. We did not observe any significant changes in the C1s spectra in the SR dose range over 100 mA h.

Dependence of the F 1*s* spectra of the F-DLC films on SR dose is shown in Fig. 7. The F peak can be decomposed into two sub-peaks, centered at 686.6 eV (—CF) and 687.4 eV (—$CF_2$) [29–31]. In the SR dose range from 0 mA h to 20 mA h, the intensity of F peak substantially decreased. In addition, the peak shifted to the lower energy side. This shift can be derived by decreasing the 687.4 eV peak intensity. In the SR dose range over 100 mA h, we did not observe any significant changes in the F 1*s* spectra.

These results showed that small doses of soft X-rays caused the —CF, —$CF_2$ and —$CF_3$ components to be desorbed or dissociated from the F-DLC film surface. On the other hand, a certain amount of fluorine remained on the film surface after surplus SR irradiation.

### *3.6. Local structure of carbon atoms in F-DLC film obtained through near-edge X-ray absorption fine structure measurements*

It is well known that NEXAFS spectroscopy using synchrotron radiation is sensitive to the local structure around the absorber atoms. NEXAFS measurements were carried out on beamline 09A (BL09A) at the NewSUBARU [32,33]. Synchrotron radiation emitted by an 11-m undulator was extracted using a varied-line-spacing plane grating and irradiated onto the sample film at the “magic angle” of 54.7° with respect to the surface. The energy resolution was estimated to be less than 0.5 eV (FWHM). The electrons coming from the sample were detected in total-electron-yield mode. The intensity of the incident X-rays was measured by detecting the photocurrent from a gold mesh. The signal strength was derived from the ratio of the photocurrent from the sample to that from the gold mesh. The NEXAFS spectra of the C *K* edge absorption were measured in the 275–335 eV range.

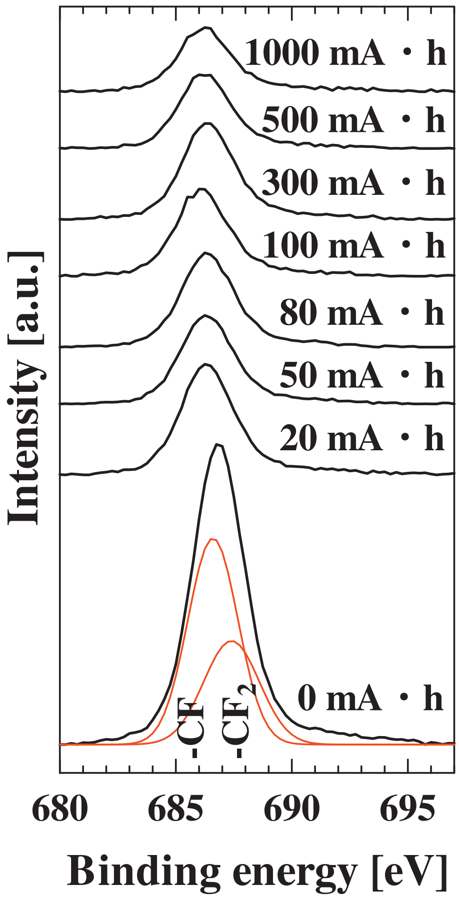


**Fig. 7.** Dependence of F 1*s* XPS spectrum of F-DLC film on SR dose.

Dependence of the C *K*-edge NEXAFS spectra of F-DLC films on SR dose is shown in Fig. 8. The sharp peak at 285.4 eV and the sub-peak at 287.6 eV respectively originate from the carbon forming $sp^2$ hybrid orbital (C═C) and the $sp^2$ carbon neighboring the F atom (C═CF) [34,35]. We observed transitions from the C 1*s* level to the unoccupied σ* states in the photon-energy region of 290 to 320 eV [36]. It was found that the sharp peak intensity at 285.4 eV increased as the SR dose but that the peak intensity at 287.6 eV decreased. In other words, the C—F bonds are dissociated and the C═C bonds are formed by the SR irradiation.

The absolute $sp^2 / (sp^2 + sp^3)$ ratio of carbon atoms in the DLC film can be determined from the C-*K* edge NEXAFS spectra of the DLC film with high accuracy, as described in Refs. 37–39. Fig. 9 shows the SR-dose dependence of the $sp^2 / (sp^2 + sp^3)$ ratio in the F-DLC film. The amount of $sp^2$ bonded carbon atoms can be extracted by normalizing the area of the resonance corresponding to the 1 s → π* transitions at 285.4 eV with a large section of the spectrum. The absolute $sp^2 / (sp^2 + sp^3)$ ratio was determined by comparing the normalized 1 s → π* area from the sample with that from the NEXAFS spectrum of the highly ordered pyrolytic graphite (HOPG) as a standard sample. The $sp^2 / (sp^2 + sp^3)$ ratio of the F-DLC film before irradiation was ≈ 0.4

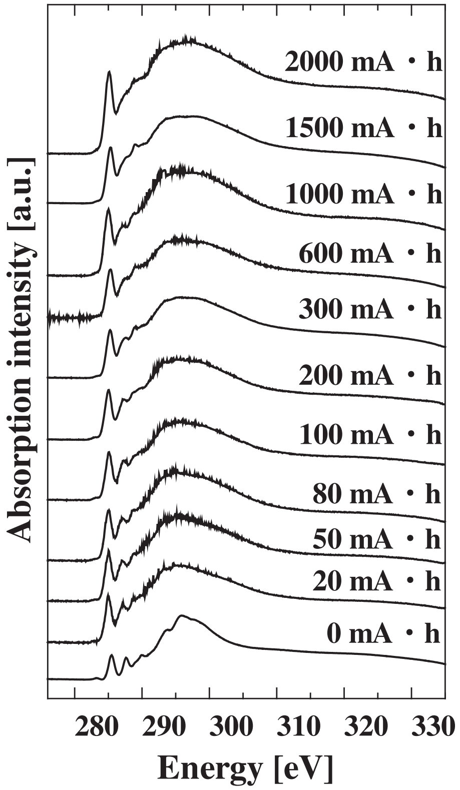


**Fig. 8.** Dependence of C *K*-edge NEXAFS spectra of F-DLC on SR dose.

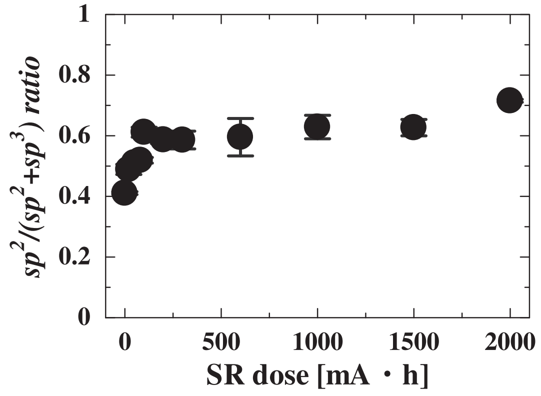


**Fig. 9.** Dependence of $sp^2$ / ($sp^2$ + $sp^3$) ratio in F-DLC film on SR dose.

and it increased rapidly to ≈ 0.6 at an SR dose of less than 100 mA h. However, at an SR dose above 100 mA h, the $sp^2$ / ($sp^2$ + $sp^3$) ratio was approximately constant at ≈ 0.6.

### 3.7. Wettability evaluated using contact angle meter

The wettability was evaluated by the contact angle of a water drop on a F-DLC film using a contact angle meter (Kyouwa Interface, Drop Master 500) with a 1 μl water drop. Fig. 10 shows the SR dose dependence of the contact angle of the F-DLC surface. The contact angle of a water drop on the F-DLC surface before irradiation was 105°, which meant it was a hydrophobic surface. It decreased substantially to ≈ 85° after 20 mA h SR exposure. At doses of more than 20 mA h, the contact angle maintained a constant ≈ 85° value, which meant the surface was hydrophilic.

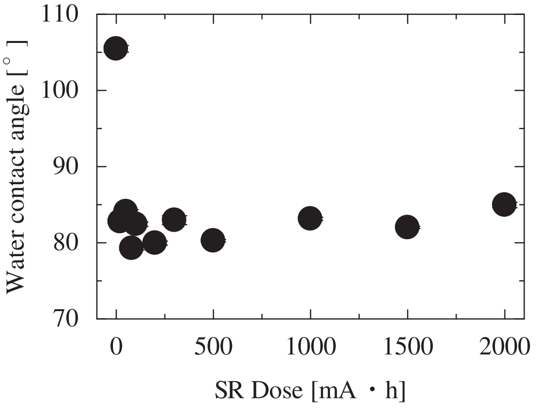


**Fig. 10.** Dependence of water drop contact angle on F-DLC film surface on SR dose measured with a contact angle meter.

### 3.8. Desorbed species from F-DLC film surface by soft X-ray irradiation

We measured the dose dependencies of species desorbed from the F-DLC film surface by using soft X-ray irradiation using a quadruple mass spectrometer (QMS) (Anelva, Q-M400QA-M) installed in the irradiation chamber of BL06. The detectable mass range was from 1 to 400, and the mass resolution was M/ΔM ≥ 200. The QMS was positioned perpendicular to the advancing direction of the soft X-ray beam. While these measurements were being taken, an incident soft X-ray beam was introduced to a sample at 45° with respect to the surface normal. We detected the species desorbed from the sample with the QMS positioned at 45° with respect to the surface normal of the sample in the opposite direction of the incident beam. We considered that the signals detected by the QMS included not only the desorbed species from the sample but also residual gas species and adsorbed species in the irradiation chamber, the substrate Si wafer and the sample. Prior to the measurement for the F-DLC films, we have measured the mass spectrum for the ion-plating DLC film (Nanotec) exposed to SR, because this film is fluorine-free and is known to be high X-ray resistivity [15]. We subtracted its values from the measured mass spectrum during the time the F-DLC films were being exposed to SR.

The mass spectrum obtained just after F-DLC film started to be irradiated by SR, which was obtained by subtracting the back-ground as described above, is shown in Fig. 11. No peaks were observed for any mass greater than 70. In Fig. 11, the peaks ascribable to the residual atmosphere in the irradiation chamber, including the vaporizing lubricant oil from the rotary pump, and the admolecules on the sample and substrate were as follows; 1($H^+$), 2($H_2^+$), 14($N^+$, $CH_2^+$), 16($O^+$, $CH_4^+$), 17($OH^+$), 18($H_2O^+$), 28($N_2^+$, $CO^+$), 32($O_2^+$) and 44($CO_2^+$). We considered that the hydrocarbon species observed at the mass numbers 13–16, 25–30, and 37–44 were not desorbed from F-DLC film but were derived from the vaporizing lubricant oil of the rotary pump. We came to this conclusion, because the mass spectrum showed that there were more hydrogen-rich species than hydrogen-poor species, though the F-DLC film used in this work contains negligible amount of hydrogen as described in Section 3.2. These are background species,

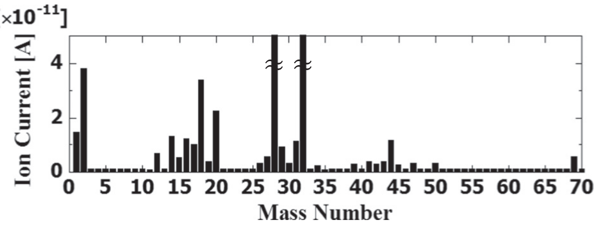


**Fig. 11.** Mass spectrum of desorbed species from F-DLC film immediately after irradiation started.

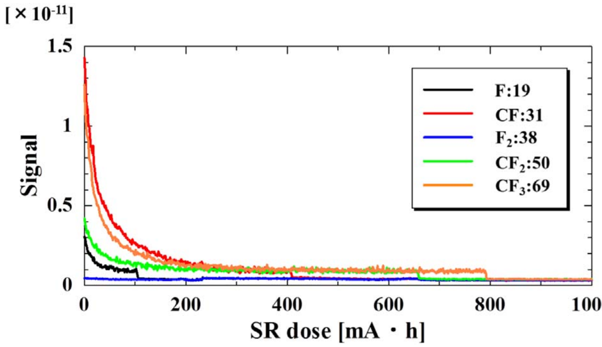


**Fig. 12.** Dependence of $F^+$, $CF^+$, $F_2{}^+$, $CF_2{}^+$, and $CF_3{}^+$ quantities from F-DLC film on SR dose.

which were not removed by subtraction, and/or species that adhered to the surface of the F-DLC films.

Several peaks can be seen in Fig. 11 which are unique to the species containing fluorine. We respectively assigned the peaks at the mass numbers 19, 20, 31, 50 and 69 to $F^+$, $HF^+$, $CF^+$, $CF_2{}^+$ and $CF_3{}^+$. In addition, we interpreted that $C^+$ at the mass number 12 is generated by the dissociation of CF, $CF_2$ and $CF_3$ in QMS, because the desorption of carbon by soft X-ray irradiation was reported to be very slow in DLC and hydrogenated DLC films [18]. The signal of $HF^+$ may be due to the combination of the fluorine which was desorbed from F-DLC film with the residual atmospheric atomic and/or molecular hydrogen in the irradiation chamber, because atomic and/or molecular hydrogen existed in abundance in the irradiation chamber from the observation of intense peaks at mass numbers 1 and 2. The peak at mass number 38, which was assigned to $F_2{}^+$, was not observed. We also found that the intensity of the peak at 19, $F^+$, was smaller than that at 30, $CF^+$. This indicated that $F^+$ was formed by the dissociation of $CF_x$ species in QMS rather than by direct desorption from F-DLC film.

Next we investigated the dose dependence of the quantity of the desorbed species. Fig. 12 shows the dose dependence of intensities of several peaks at the mass numbers 19, 31, 38, 50, and 69, which respectively corresponded to $F^+$, $CF^+$, $F_2{}^+$, $CF_2{}^+$, and $CF_3{}^+$.

Large quantities of fluorocarbon species were emitted from the F-DLC film at the same time that the soft X-ray irradiation was started. The quantity of desorbed species decreased exponentially as the SR dose was increased in the range of 0–100 mA h and became approximately constant at a very small value with an SR dose of more than 300 mA h. The observations we depicted in Figs. 11 and 12 indicate that the dominant species from F-DLC film produced by the SR irradiation were $CF_x$, especially CF and $CF_3$. These results greatly differed from the results obtained when H-DLC film was subjected to SR irradiation [18]. In the latter case, carbon was not desorbed and only hydrogen was desorbed as H and $H_2$.

### 3.9. Surface modification process of F-DLC film by soft X-ray irradiation

As described in the above sections, we observed that soft X-ray irradiation caused various surface and bulk properties of F-DLC films to change. The contact angle of the F-DLC film surface decreased significantly from 105° to 85° after 20 mA h SR exposure. This decrease was dominantly ascribable to the decreased F component on the F-DLC film surface, which was observed in the XPS spectra. This phenomenon can be related to the fact that SR irradiation does not change the film flatness, as we observed using AFM. Film density also decreased substantially after 20 mA h SR exposure. This decrease was interpreted to desorption of the fluorocarbon species, dominantly $CF_3$, from surface neighborhood of F-DLC film. On the other hand, bulk properties - elemental composition of film, film thickness and $sp^2/(sp^2+sp^3)$ ratio of carbon atoms - increased as the SR dose and became approximately constant with an SR dose of more than 300 mA h. These dose dependences agreed with those of the signal intensity of $CF_x$ species estimated using QMS. Therefore, changes in these properties due to soft X-ray irradiation were undoubtedly related to desorption of $CF_x$ species from the F-DLC films.

The modification process on the F-DLC film by the irradiation of SR can be considered as follows: (1) Carbon and fluorine atoms in the F-DLC film were excited by the soft X-rays. (2) Carbon-carbon bonding, which bonded to fluorine atoms, was decoupled and $CF_x$ species were desorbed from the F-DLC films. As discussed in Section 3.8, the desorbed species from F-DLC film were dominant for CF and $CF_3$, not for F or $F_2$. The desorbed species greatly differed from those obtained when H-DLC films were subjected to SR irradiation, in which carbon was not desorbed and only hydrogen was desorbed as H and $H_2$. We consider that this disagreement is ascribable to the fact that bonding energy of C—F, 130.8 kcal/mol, was larger than that of C—H in the F-DLC film. For reference, the bond energies of C—F in $CF_4$ and C—H in $CH_4$ have been respectively reported to be 130.8 kcal/mol and 104.3 kcal/mol [40]. (3) Desorption of $CF_x$ species caused decreases in film thickness, and film density, because F atoms were heavier than C atoms. (4) Decoupled $CF_x$ species were desorbed, while the remaining carbon atoms coupled with neighboring carbon atoms. The $sp^2/(sp^2+sp^3)$ ratio of carbon atoms in F-DLC film increased because carbon-carbon double bonds were formed with a certain ratio in this coupling. (5) The reactions stated above were not caused, when the fluorine ratio in an F-DLC film decreased as a consequence of SR irradiation. Therefore, film thickness stopped decreasing in the SR dose range over 300 mA h. In other words, this layer with a little fluorine ratio has X-ray tolerance. Therefore, F-DLC film X-ray durability was improved after the SR irradiation at a 300 mA h dose. In addition, the F-DLC film, which had X-ray durability, contained ≈ 10% of fluorine atoms on the surface and ≈ 20% of fluorine atoms in the film.

The penetration depth of SR radiation, in particular the soft X ray, may be several microns. Therefore, the dissociation of chemical bonds may occur in the bulk region of films to form, possibly, F atoms. These F atoms may recombine with dangling bonds in F-DLC film generated by the SR irradiation. These dissociation and recombine processes may lead F atoms (or F-containing species) to have certain fluidity. On the other hand, these species may fly away from the surface of films. Therefore, a diffusion process of the fluorinated fragments from the bulk to the surface may be expected. It seems that the saturation of the elemental ratio in the region of higher SR dose has the origin in the equilibrium of the dissociation and recombination due to, probably, a low diffusion coefficient.

## 4. Conclusion

We investigated the effects of soft X-ray radiation on fluorinated DLC films. Diamond-like carbon film is known as a material that is tolerant to X-rays, but DLC film with high fluorine content was found to be etched and affected by soft X-ray irradiation. We found that surface flatness was maintained but that various material and structural properties varied as the SR dose was varied. These properties included density, elemental composition on the film surface and in the film, local structure of carbon atom, and wettability. These changes are caused by desorption of fluorocarbon from F-DLC films. This situation has been completely different from the irradiation of hydrogenated DLC films, whose dominant desorbed species is hydrogen without carbon. Fluorocarbon groups are desorbed by excitation due to soft X-ray irradiation, and the remaining carbon atoms bond to each other. As a result, $sp^2/(sp^2+sp^3)$ ratio of carbon atoms in F-DLC film increase. The etching and modification processes do not proceed after the irradiation of SR with more than 300 mA h. At this point, the percentage of fluorine atoms in F-DLC films is about 10%. This means that such films have sufficient durability with respect to soft X-rays. It can therefore be expected that they can be used as means to provide anticorrosion coating under soft X-ray irradiation in various industrial fields.

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