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## Resistance of Hydrogenated Titanium-Doped Diamond-Like Carbon Film to Hyperthermal Atomic Oxygen

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**Abstract:** The effect of irradiation by a hyperthermal-atomic-oxygen beam on hydrogenated titanium-doped diamond-like carbon (hydrogenated Ti-DLC) films, applied as a solid lubricant for equipment used in low-earth orbit was investigated. Unlike the film thickness of hydrogenated non-doped DLC films, that of hydrogenated Ti-DLC films was found to be constant after the films were exposed to atomic oxygen. In addition, bulk composition of the hydrogenated Ti-DLC film stayed constant, and in particular, hydrogen content in the film did not decrease. These results indicate that a hydrogenated Ti-DLC film can keep its low friction properties under vacuum. Surface chemical analysis showed that a titanium-oxide layer is formed on the film by exposure to atomic oxygen. The thickness of the titanium oxide layer was estimated to be about 5 nm from the element distribution in the depth direction of the hydrogenated Ti-DLC films. The titanium-oxide

layer was interpreted to protect the bulk film from erosion by hyperthermal atomic oxygen.

**Keywords:** titanium-doped diamond-like carbon film; solid lubricant; hyperthermal atomic-oxygen beam; Rutherford backscattering spectrometry; elastic-recoil detection analysis; X-ray photoelectron spectroscopy; near-edge X-ray-absorption fine structure; glow-discharge optical-emission spectroscopy

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## 1. Introduction

In space, solid lubricants are required to replace oil, because oil evaporates and freezes in such an environment. To use lubricant in space, their resistances to the extreme environment of space, namely, ultra-high vacuum, high temperature, ultraviolet light and X-rays, atomic oxygen, and their synergistic effects, must be improved. Most artificial satellites are positioned in the region called the “low-earth orbit” (LEO), which is less than 2000 km above the ground. In the LEO, hyperthermal atomic oxygen is the dominant species and the main cause of deterioration in the properties of astronautical materials [1–4]. Solid lubricant used in artificial satellites must therefore have sufficient resistance against irradiation by atomic oxygen.

Diamond-like carbon (DLC) films are amorphous carbon films and have been used in the tribological field as a coating material on edged-tools, computer hard disks, and automobile components because they have a wide range of excellent properties including low friction coefficient, high hardness, and good corrosion resistance [5–10]. Hydrogenated DLC films were expected to be used as lubricants in LEO, because it was known that DLC films with a hydrogen content greater than 40 at.% provide ultra-low friction (friction coefficient less than 0.001) even under air and vacuum conditions [11]. However, we previously reported that hydrogenated DLC films are etched by the collision with hyperthermal atomic oxygen [12]. As a result, hydrogenated DLC films cannot be used as a solid lubricant in space as is.

In the last decade, many working groups reported that several properties of DLC films are improved by doping with a “hetero element” [13–27]. Especially, titanium (Ti)-doped DLC films have been widely investigated because they are expected to improve sliding properties, burning resistance, and oxidation resistance [22–27]. In a previous study, we investigated the effect of irradiation by a hyperthermal atomic-oxygen beam on hydrogenated a Ti-doped diamond-like carbon (Ti-DLC) film [28]. Under the irradiation of atomic oxygen, carbon atoms were desorbed from the hydrogenated Ti-DLC films and formed gas species (CO and/or CO<sub>2</sub>), and oxygen atoms and titanium atoms were found to generate titanium oxide on the surface of the films. However, the surface-modification mechanism cannot be observed, because the fluence of atomic oxygen was too high. As for a more important point regarding use as a solid lubricant, the variation of bulk properties of a hydrogenated Ti-DLC film has not been confirmed. In this study, the purpose to clarify the hydrogenated Ti-DLC film used as a solid lubricant in space, dependence of surface and bulk properties of a hydrogenated Ti-DLC film irradiated by a hyperthermal atomic-oxygen beam on fluence was investigated. In particular, hydrogenated Ti-DLC films were exposed to atomic oxygen with a collisional energy of 5 eV by using a laser-detonation beam apparatus. Film thickness and bulk composition of the

hydrogenated Ti-DLC film were estimated by a combination of Rutherford backscattering spectrometry (RBS) and elastic-recoil detection analysis (ERDA). The chemical analysis on the DLC film surface was performed by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray-absorption fine structure (NEXAFS). Element distribution in depth direction was determined by the glow-discharge optical-emission spectroscopy (GD-OES).

## 2. Experimental Section

The hydrogenated Ti-DLC films used in this study, commercially available from Nippon ITF, were deposited to a thickness of 400 nm on silicon wafers using amplitude modulated RF plasma-enhanced chemical-vapor deposition (PECVD) [29], which hydrogen content was greater than 40 at.%. The hydrogenated Ti-DLC films were exposed to hyperthermal atomic oxygen by a laser-detonation beam apparatus [12,30,31]. Pure oxygen gas was introduced into the nozzle throat through a pulsed supersonic valve. A pulse from a CO<sub>2</sub> laser (wavelength: 10.6 μm, laser power: >5 J/pulse) was focused onto the oxygen gas at the nozzle throat. By absorbing the laser energy, high-density and high-temperature oxygen plasma was formed at the nozzle throat. Once the plasma was formed, it propagated and absorbed the energy in the tail of the laser pulse. The plasma propagated along the incident laser axis, and oxygen molecules were decomposed and accelerated at the shock front of the propagating plasma. The atomic-oxygen beam was irradiated perpendicularly onto the sample surface at room temperature. The dependence of the surface reaction of the hyperthermal atomic oxygen beam sample on the sample temperature is little known, because the irradiated oxygen atoms have translation energy of approximately 50,000 degrees [31]. The typical atomic oxygen flux at the sample position (46 cm from the nozzle) was estimated to be  $3.51 \times 10^{15}$  atoms cm<sup>-2</sup>s<sup>-1</sup> by using a silver-coated quartz-crystal microbalance (QCM). The average translational energy of hyperthermal atomic oxygen was estimated to be 5.46 eV by using a time-of-flight (TOF) measurement system consisting of a quadrupole mass spectrometer with a scintillation detector and a multichannel scalar. This energy is the same as the atomic oxygen energy in the LEO [1–4]. In the present study, six sheets of hydrogenated Ti-DLC film were exposed to a hyperthermal-atomic-oxygen beam corresponding to fluences of 0,  $1.2 \times 10^{17}$ ,  $1.2 \times 10^{18}$ ,  $3.5 \times 10^{18}$ ,  $1.2 \times 10^{19}$ , and  $1.2 \times 10^{20}$  atoms cm<sup>-2</sup>. The fluence step of the atomic oxygen beam was made smaller than that of a previous work [28] so that the reaction mechanism on the surface of hydrogenated Ti-DLC films could be investigated.

Film thickness and bulk composition of the hydrogenated Ti-DLC film were estimated by a combination of ERDA and RBS. These measurements were performed using a tandem electrostatic accelerator (5SDH, National Electrostatic Corporation, Middleton, WI, USA) located in the Faculty of Maritime Sciences, Kobe University [12,32]. The sample was irradiated by a 4.2 MeV He<sup>2+</sup> beam to accelerate the negative ions of helium (<sup>4</sup>He) generated by the RF-discharge negative-charge-exchange ion source. The incident angle of the beam was 15 ° with respect to the surface of the sample. As for the RBS, high-energy He<sup>2+</sup> ions, scattered elastically by the sample, were captured with a solid-state detector (SSD) positioned at 160 ° with respect to the beam direction. As for the ERDA, He<sup>2+</sup> 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.

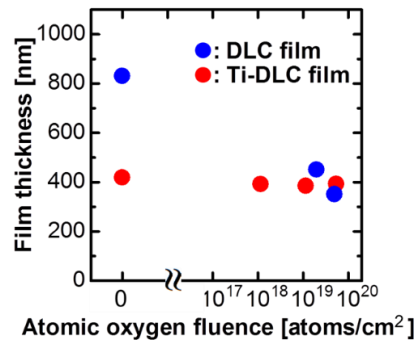
Elementary composition of the hydrogenated Ti-DLC film surface was estimated by a conventional X-ray photoelectron spectroscopy (XPS) apparatus (Shimadzu, ESCA-1000, Kyoto, Japan) mounted with a hemispherical electron energy analyzer. The Mg  $K\alpha$  line (1253.6 eV), used as the X-ray source, was incident at  $45^\circ$  with respect to the surface normal. The emission angle was  $45^\circ$  with respect to the incident angle.

NEXAFS measurements were carried out on beamline 09A (BL09A) at the NewSUBARU synchrotron-radiation facility in University of Hyogo, which has a 1.5-GeV electron-storage ring [33–36]. 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  $54.7^\circ$  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, Ti  $L$  absorption, and O  $K$  absorption were measured in the range 275–300 eV, 450–480 eV, and 520–560 eV, respectively.

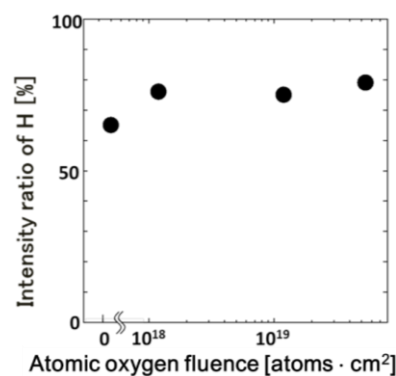
Element distribution in depth direction of the hydrogenated Ti-DLC films was estimated by glow-discharge optical-emission spectroscopy (GD-OES) performed using a GD-Profilier2 (HORIBA, Kyoto, Japan). The sample was sputtered by argon plasma. Quantitative-chemical-depth profiles were estimated by detecting atomic emission from sputtering atoms.

### 3. Results and Discussion

Film thickness and bulk composition containing hydrogen of the hydrogenated Ti-DLC films were analyzed by a combination of RBS and ERDA. Dependence of film thickness (determined by measuring the hydrogenated Ti-DLC films by RBS) on atomic-oxygen beam fluence is shown in Figure 1. The red circles represent thickness of the hydrogenated Ti-DLC film. Film thicknesses of a hydrogenated non-doped DLC film, which were estimated in our previous study [12], are shown for reference. According to the figure, thickness of the hydrogenated non-doped DLC film decreased from 800 to 350 nm by irradiation of atomic oxygen with fluence of  $5.0 \times 10^{19}$  atoms  $\text{cm}^{-2}$ . On the other hand, thickness of the hydrogenated Ti-DLC film was found to be constant,  $\cong 400$  nm, after exposure to atomic oxygen with fluence of more than  $5.0 \times 10^{19}$  atoms  $\text{cm}^{-2}$ . These results demonstrate that the doping with titanium atoms gives the hydrogenated DLC films high etching tolerance against exposure to atomic oxygen. The dependence of relative hydrogen content in the film on atomic oxygen beam fluence was estimated by comparing the signal intensity of hydrogen in the ERDA spectra with that of carbon in the RBS spectra. Dependence of intensity ratio of hydrogen in the hydrogenated Ti-DLC films on atomic-oxygen beam fluence is shown in Figure 2. It is clear from the figure that the hydrogen ratio did not decrease after the film was exposed to atomic oxygen. That is to say, hydrogen is not desorbed from the hydrogenated Ti-DLC films by the irradiation with atomic oxygen. This result indicates that the hydrogen content in the hydrogenated Ti-DLC film exceeded 40% after the irradiation with atomic oxygen. A hydrogenated Ti-DLC film is therefore expected to exhibit low-friction properties in a vacuum.



**Figure 1.** Dependence of film thickness determined from Rutherford backscattering spectrometry (RBS) of titanium-doped diamond-like carbon (Ti-DLC) films (red circles) and non-doped DLC films (blue circles) on atomic-oxygen fluence.

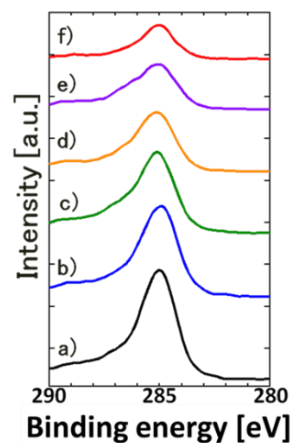


**Figure 2.** Dependence of relative hydrogen content determined from combination of RBS and elastic-recoil detection analysis (ERDA) in Ti-DLC films on atomic-oxygen fluence.

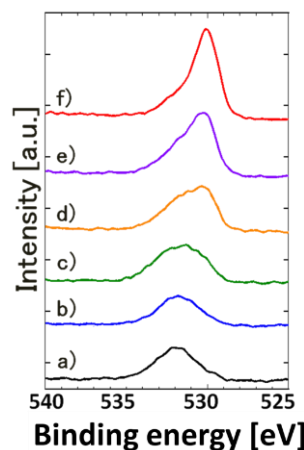
Surface chemical analysis on hydrogenated Ti-DLC films was performed by XPS and NEXAFS study. In our previous work, change of surface chemical states could not be traced, because the step in atomic-oxygen fluence was too large. Only XPS spectra over a wide range were reported; the detailed structure of each peak in the XPS spectra was not discussed [28]. In the present study, the fluence of an atomic-oxygen beam irradiated onto a hydrogenated Ti-DLC film was varied in smaller steps. In Figures 3–8, atomic-oxygen-beam fluences are (a) 0, (b)  $1.2 \times 10^{17}$ , (c)  $1.2 \times 10^{18}$ , (d)  $3.5 \times 10^{18}$ , (e)  $1.2 \times 10^{19}$ , and (f)  $1.2 \times 10^{20}$  atoms  $\text{cm}^{-2}$ .

Change in elementary composition of the surface of hydrogenated Ti-DLC films due to the exposure to an atomic oxygen beam was investigated by XPS. Dependence of the C1s spectra of hydrogenated Ti-DLC films on fluence is shown in Figure 3. It is clear from figure that intensity of the peak at 285 eV decreased with increasing fluence of atomic oxygen. This result means that the amount of carbon atoms on the surface of hydrogenated Ti-DLC film is decreased by irradiation with atomic oxygen. Dependence of the O1s spectra of the hydrogenated Ti-DLC films on fluence is shown in Figure 4. The O1s peak at 532 eV is still observable in spectrum (a) [0 atoms  $\text{cm}^{-2}$ ]. It is ascribed to natural oxidation at the surface of the hydrogenated Ti-DLC film. The peak at 530 eV increases with increasing atomic-oxygen fluence, and it is assigned to the Ti–O bond [37]. This result indicates that the amount of oxygen atoms at the surface of the hydrogenated Ti-DLC film is increased by the irradiation by atomic oxygen. Dependence of the Ti 2p spectra of the hydrogenated Ti-DLC films on

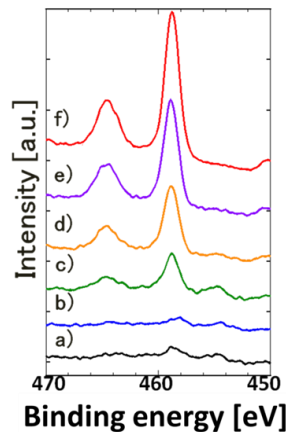
fluence is shown in Figure 5. The Ti 2p peak is not observed in spectra (a) [ $0 \text{ atoms cm}^{-2}$ ] and (b) [ $1.2 \times 10^{17} \text{ atoms cm}^{-2}$ ]. However, the peaks at 460 eV and 465 eV, which were derived from  $\text{TiO}_2$  [37], increase with increasing atomic-oxygen fluence. The results of estimations by elementary analysis, which took into account a relative-sensitivity coefficient, are listed in Table 1. From the above-described XPS results, the amount of titanium and oxygen atoms in the hydrogenated Ti-DLC films increases with increasing atomic oxygen fluence. However, the amount of carbon atoms decreases monotonically. These changes in peak intensity and peak profile are observed for the peaks of spectra (a) [ $0 \text{ atoms cm}^{-2}$ ] to (e) [ $1.2 \times 10^{19} \text{ atoms cm}^{-2}$ ]. On the other hand, the difference is hardly observed for every peak of spectra (e) [ $1.2 \times 10^{19} \text{ atoms cm}^{-2}$ ] and (f) [ $1.2 \times 10^{20} \text{ atoms cm}^{-2}$ ]. Accordingly, change in surface composition due to the irradiation by atomic oxygen is regarded to be completed by the irradiation with fluence of  $1.2 \times 10^{19} \text{ atoms cm}^{-2}$ .



**Figure 3.** C 1s XPS spectra of Ti-DLC films before and after exposure to atomic oxygen. Fluences of atomic oxygen beam are (a)  $0 \text{ atoms cm}^{-2}$ , (b)  $1.2 \times 10^{17} \text{ atoms cm}^{-2}$ , (c)  $1.2 \times 10^{18} \text{ atoms cm}^{-2}$ , (d)  $3.5 \times 10^{18} \text{ atoms cm}^{-2}$ , (e)  $1.2 \times 10^{19} \text{ atoms cm}^{-2}$ , and (f)  $1.9 \times 10^{20} \text{ atoms cm}^{-2}$ .



**Figure 4.** O 1s XPS spectra of Ti-DLC films before and after exposure to atomic oxygen. Fluences of atomic oxygen beam are (a)  $0 \text{ atoms cm}^{-2}$ , (b)  $1.2 \times 10^{17} \text{ atoms cm}^{-2}$ , (c)  $1.2 \times 10^{18} \text{ atoms cm}^{-2}$ , (d)  $3.5 \times 10^{18} \text{ atoms cm}^{-2}$ , (e)  $1.2 \times 10^{19} \text{ atoms cm}^{-2}$ , and (f)  $1.9 \times 10^{20} \text{ atoms cm}^{-2}$ .



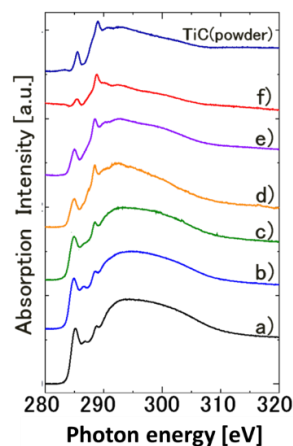
**Figure 5.** Ti 2p XPS spectra of Ti-DLC films before and after exposure to atomic oxygen. Fluences of atomic oxygen beam are (a) 0 atoms cm<sup>-2</sup>, (b)  $1.2 \times 10^{17}$  atoms cm<sup>-2</sup>, (c)  $1.2 \times 10^{18}$  atoms cm<sup>-2</sup>, (d)  $3.5 \times 10^{18}$  atoms cm<sup>-2</sup>, (e)  $1.2 \times 10^{19}$  atoms cm<sup>-2</sup>, and (f)  $1.9 \times 10^{20}$  atoms cm<sup>-2</sup>.

**Table 1.** Elementary composition of Ti-DLC films before and after exposure to atomic oxygen.

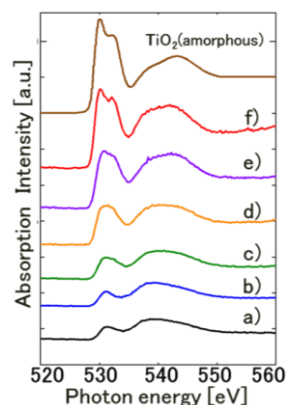
Fluence	C	O	Ti
atoms cm <sup>-2</sup>		at. %	
0	79	18	3
$1.16 \times 10^{17}$	77	19	4
$1.16 \times 10^{18}$	68	25	7
$3.52 \times 10^{18}$	59	29	13
$1.16 \times 10^{19}$	44	38	18
$2.74 \times 10^{19}$	37	36	27
$5.47 \times 10^{19}$	35	35	30
$8.3 \times 10^{19}$	22	40	38
$1.85 \times 10^{20}$	24	41	35

Change of the local structure of a hydrogenated Ti-DLC film due to exposure to atomic oxygen was previously discussed on the basis of the NEXAFS measurements [38]. NEXAFS spectroscopy using synchrotron radiation is known to be sensitive to the local structure around the absorber atoms. Dependence of the C *K*-edge NEXAFS spectra of hydrogenated Ti-DLC films on fluence is shown in Figure 6. The spectrum of a TiC powder is also shown for reference. The pre-edge resonance at 285.4 eV originates from sp<sup>2</sup> (C=C) sites [12,36]. The transitions from C 1s level to unoccupied σ\* states are observed in the photon-energy region of 290 to 320 eV. Intensity of the sharp peak at 285.4 eV decreases with increasing atomic-oxygen fluence. On the other hand, intensity of the peak at 289 eV, which was assigned to C–O bonds [39], increases. In other words, the C–C bonds are changed to C–O bonds by irradiation with atomic oxygen. Dependence of the O *K*-edge NEXAFS spectra of hydrogenated Ti-DLC films on fluence is shown in Figure 7. The spectrum of a TiO<sub>2</sub> amorphous film is also shown for reference [40]. A peak is observable in spectrum (a) [0 atoms cm<sup>-2</sup>]. It is due to natural oxidation at the surface of the hydrogenated Ti-DLC film as described in XPS results. With increasing atomic-oxygen fluence, intensity of the peak derived from TiO<sub>2</sub> increases. Ti *L*-edge

NEXAFS spectra of the hydrogenated Ti-DLC films, before and after exposure to atomic oxygen, are shown in Figure 8. The spectra of TiC powder and amorphous TiO<sub>2</sub> are also shown for reference [40]. The spectrum of the non-irradiated hydrogenated Ti-DLC film almost accords with that of TiC powder. Intensity of the peak derived from TiO<sub>2</sub> increases with increasing fluence of atomic oxygen. In other words, the Ti–C bonds are changed to Ti–O bonds by atomic oxygen irradiation. These results indicate that the C–C bonds in the surface neighborhood are changed to C–O bonds and that the Ti–C bonds in the surface neighborhood are changed to Ti–O bonds by atomic-oxygen irradiation. In other words, a titanium-oxide layer is formed on the surface of the hydrogenated Ti-DLC films by atomic-oxygen irradiation. This oxide layer is considered to protect the bulk film from erosion by hyperthermal atomic oxygen. In accord with the XPS results, various changes in NEXAFS spectra (a) [0 atoms cm<sup>−2</sup>] to (e) [ $1.2 \times 10^{19}$  atoms cm<sup>−2</sup>] are observed, but little difference in spectra (e) [ $1.2 \times 10^{19}$  atoms cm<sup>−2</sup>] and (f) [ $1.2 \times 10^{20}$  atoms cm<sup>−2</sup>].

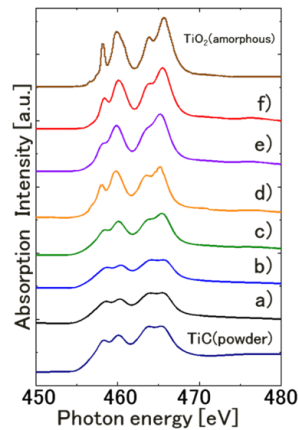


**Figure 6.** NEXAFS spectra of the C *K*-edge, before and after exposure to atomic oxygen. Fluences of atomic oxygen beam are (a) 0 atoms cm<sup>−2</sup>, (b)  $1.2 \times 10^{17}$  atoms cm<sup>−2</sup>, (c)  $1.2 \times 10^{18}$  atoms cm<sup>−2</sup>, (d)  $3.5 \times 10^{18}$  atoms cm<sup>−2</sup>, (e)  $1.2 \times 10^{19}$  atoms cm<sup>−2</sup>, and (f)  $1.9 \times 10^{20}$  atoms cm<sup>−2</sup>. The spectrum of TiC powder is also shown for reference.



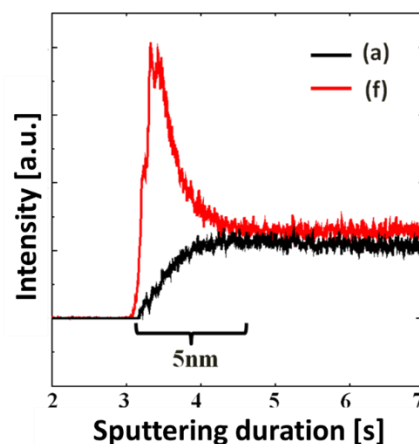
**Figure 7.** NEXAFS spectra of the O *K*-edge, before and after exposure to atomic oxygen. Fluences of atomic oxygen beam are (a) 0 atoms cm<sup>−2</sup>, (b)  $1.2 \times 10^{17}$  atoms cm<sup>−2</sup>, (c)  $1.2 \times 10^{18}$  atoms cm<sup>−2</sup>, (d)  $3.5 \times 10^{18}$  atoms cm<sup>−2</sup>, (e)  $1.2 \times 10^{19}$  atoms cm<sup>−2</sup>, and (f)  $1.9 \times 10^{20}$  atoms cm<sup>−2</sup>. The spectrum of a TiO<sub>2</sub> amorphous is also shown for reference.



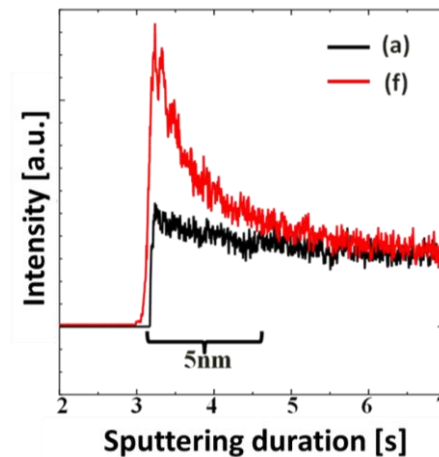


**Figure 8.** NEXAFS spectra of the Ti *L*-edge, before and after exposure to atomic oxygen. Fluences of atomic oxygen beam are (a) 0 atoms cm<sup>-2</sup>, (b)  $1.2 \times 10^{17}$  atoms cm<sup>-2</sup>, (c)  $1.2 \times 10^{18}$  atoms cm<sup>-2</sup>, (d)  $3.5 \times 10^{18}$  atoms cm<sup>-2</sup>, (e)  $1.2 \times 10^{19}$  atoms cm<sup>-2</sup>, and (f)  $1.9 \times 10^{20}$  atoms cm<sup>-2</sup>. The spectra of TiC powder and TiO<sub>2</sub> amorphous are also shown for reference.

To estimate the thickness of titanium-oxide layer formed by the irradiation of atomic oxygen, element distribution in the depth direction of the hydrogenated Ti-DLC films was measured by GD-OES. Element analysis results (in the depth direction) for titanium and oxygen in the hydrogenated Ti-DLC films are shown in Figures 9 and 10 respectively. In both figures, the black line and red line show the analysis results for elements in the depth direction of the hydrogenated Ti-DLC films exposed to atomic oxygen with fluences of (a) 0 atoms cm<sup>-2</sup> and (f)  $1.2 \times 10^{20}$  atoms cm<sup>-2</sup>, respectively. As for Figure 9, the amount of titanium in the surface neighborhood of the hydrogenated Ti-DLC film (*i.e.*, depth of less than 5 nm) before irradiation is small. However, it was increased in this region by irradiation of atomic oxygen. As shown in Figure 10, the amount of oxygen in the 5-nm-deep region was increased by irradiation of atomic oxygen. It is concluded from these results that the thickness of the titanium-oxide layer formed on the film surface by irradiation of atomic oxygen is about 5 nm.



**Figure 9.** Element analysis (in depth direction) of titanium in Ti-DLC films. Fluence of atomic oxygen is (a) 0 atoms cm<sup>-2</sup> and (f)  $1.9 \times 10^{20}$  atoms cm<sup>-2</sup>.



**Figure 10.** Element analysis (in depth direction) of oxygen in Ti-DLC films.

According to the above-described experimental results, the resistance of hydrogenated Ti-DLC films to atomic oxygen can be explained as follows. Film thickness and hydrogen content of the hydrogenated Ti-DLC films become constant after sufficient irradiation with atomic oxygen. This result differs from that reported in the case of non-doped hydrogenated DLC films [12]. Hydrogenated Ti-DLC films have resistance to etching by hyperthermal-atomic-oxygen irradiation, so they are expected to keep low-friction properties in a vacuum, because the hydrogen content in the film exceeded 40% after the irradiation. This result demonstrates that hydrogenated Ti-doped DLC films are useful as a lubricant for use in the LEO. The XPS study showed that the amounts of titanium and oxygen atoms in the surface of the hydrogenated Ti-DLC films increases, while the amount of carbon atoms decreases, with increasing fluence of atomic oxygen. The NEXAFS study showed that C–C bonds and Ti–C bonds in the surface neighborhood are changed to C–O bonds and Ti–O bonds, respectively, by atomic-oxygen irradiation. These XPS and NEXAFS results indicate that titanium-oxide layer forms on the surface of hydrogenated Ti-DLC films by irradiation with atomic oxygen. Namely, carbon atoms on the hydrogenated Ti-DLC film surface desorb from the films to form gas species (CO and/or CO<sub>2</sub>), and the titanium atoms remain on the surface of the film and generate nonvolatile titanium oxide. The resistance of hydrogenated Ti-DLC films to atomic oxygen can be ascribed to this titanium-oxide layer formed on the surface by irradiation with atomic oxygen. This titanium-oxide layer is formed by irradiation of atomic oxygen with fluence of  $1.2 \times 10^{19}$  atoms cm<sup>−2</sup>. The fluence of atomic oxygen in the LEO region was estimated to be  $2.3 \times 10^{20}$  atoms cm<sup>−2</sup> to  $6.6 \times 10^{21}$  atoms cm<sup>−2</sup> peryear [41]. In the LEO region, it therefore takes 16 h to 19 days to form titanium-oxide layer as a protective coating against irradiation by atomic oxygen. The thickness of the titanium-oxide layer, formed on the surface by irradiation with atomic oxygen, was found to be about 5 nm by GD-OES. Generally, solid lubricants function by surface exfoliating. It is therefore concluded that a titanium-oxide layer with thickness of 5 nm will not degrade the friction properties of solid lubricants.

#### 4. Conclusions

Application of hydrogenated Ti-DLC films as a usable solid lubricant of components in artificial satellites positioned in the LEO region was investigated, and the resistance of hydrogenated Ti-DLC

films to irradiation by hyperthermal atomic oxygen was evaluated. This investigation demonstrated that hydrogenated Ti-DLC films have etching tolerance to irradiation by hyperthermal-atomic-oxygen. Accordingly, hydrogenated Ti-DLC films can be expected to exhibit low-friction properties under vacuum, because the hydrogen content in the film does not decrease after the film is exposed to atomic oxygen. These resistances were ascribable to a titanium-oxide layer formed on the surface of the hydrogenated Ti-DLC films by irradiation with atomic oxygen. Forming the titanium-oxide layer in the LEO region was estimated to take 16 h to 19 days. The thickness of the titanium-oxide layer formed was found to 5 nm, which can be regarded as not having any influence on the lubricity of the lubricant. It is concluded from these results, that a hydrogenated Ti-DLC film can function as a solid lubricant in the LEO region. In future work, it is planned to examine the friction coefficient of the hydrogenated Ti-DLC film after it is exposed to atomic oxygen.

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### Author Contributions

K. Kidena conceived and designed the experiments under the instruction of K. Kanda. M. Endo and H. Takamatsu helped K. Kidena to perform the experiments. Especially, H. Takamatsu took over this work after the graduation of K. Kidena. M. Niibe helped with acquiring the NEXAFS spectra at NewSUBARU BL09A and discussed on the results. M. Tagawa, K. Yokota and Y. Furuyama obtained the ERDA and RBS spectra by a tandem electrostatic accelerator (5SDH), analyzed these data, and gave their general arguments concerning the study. K. Komatsu and H. Saitoh acquired the GD-OES spectra and interpreted the results.

### Conflicts of Interest

The authors declare no conflict of interest.

### References

1. Crutcher, E.R.; Nishimura, L.S.; Warner, K.J.; Wascher, W.W. Silver Teflon Blanket: LDEF Tray C-08. In Proceedings of LDEF-69 Months in Space: First Post-Retrieval Symposium, Kissimmee, FL, USA, 2–8 June 1991; 861–874.
2. Banks, B.A.; de Groh, K.K.; Miller, S.K. Low Earth Orbital Atomic Oxygen Interactions with Spacecraft Materials. In Proceedings of the 2004 Fall Meeting, Boston, MA, USA, November 29–December 3, 2004; 1–12.
3. Han, J.H.; Kim, C.G. Low earth orbit space environment simulation and its effects on graphite/epoxy composites. *Compos. Struct.* **2006**, *72*, 218–226.
4. Samwel, S.W. Low Earth Orbit Atomic Oxygen Erosion Effect on Spacecraft Materials. *Space Res. J.* **2014**, *7*, 1–13.

5. Aisenberg, S.; Chabot, S. Deposition of carbon films with diamond properties. *Carbon* **1972**, *10*, 356.
6. Robertson, J. Properties of diamond-like carbon. *Surf. Coat. Technol.* **1992**, *50*, 185–203.
7. Robertson, J. Diamond-like amorphous carbon. *Mater. Eng. R* **2002**, *37*, 129–281.
8. Podogornik, B.; Vizintin, J. Tribological reaction between oil additives and DLC coatings for automotive applications. *Surf. Coat. Technol.* **2005**, *200*, 1982–1989.
9. Bewilogua, K.; Hofmann, D. History of diamond-like carbon films—from first experiments to worldwide applications. *Surf. Coat. Technol.* **2014**, *242*, 214–225.
10. Luo, J.K.; Fu, Y.Q.; Le, H.R.; Williams, J.A.; Spearing, S.M.; Milne, W.I. Diamond and diamond-like carbon MEMS. *J. Micromech. Microeng.* **2007**, *17*, S147–S163.
11. Donnet, C.; Belin, M.; Auge, J.C.; Martin, J.M.; Grill, A.; Patel, V. Tribochemistry of diamond-like carbon coatings in various environments. *Surf. Coat. Technol.* **1994**, *68–69*, 626–631.
12. Tagawa, M.; Kumiko, K.; Kitamura, A.; Matsumoto, K.; Yoshigoe, A.; Teraoka, Y.; Kanda, K.; Niibe, M. Synchrotron radiation photoelectron spectroscopy and near-edge X-ray absorption fine structure study on oxidative etching of diamond-like carbon films by hyperthermal atomic oxygen. *Appl. Surf. Sci.* **2010**, *256*, 7678–7683.
13. Oguri, K.; Arai, T. Tribological properties and characterization of diamond-like carbon coatings with silicon prepared by plasma-assisted chemical vapor deposition. *Surf. Coat. Technol.* **1991**, *47*, 710–721.
14. Voevodin, A.A.; Rebholz, C.; Matthews, A. Comparative tribology studies of hard ceramic and composite metal-DLC coatings in sliding friction conditions. *Tribol. Trans.* **1995**, *38*, 829–836.
15. Silva, S.R.P.; Robertson, J.; Amaratunga, G.A.J. Nitrogen modification of hydrogenated amorphous carbon films. *J. Appl. Phys.* **1997**, *81*, 2626–2634.
16. Kim, M.; Lee, K.; Eun, K. Tribological behavior of silicon-incorporated diamond-like carbon films. *Surf. Coat. Technol.* **1999**, *112*, 204–209.
17. Varma, A.; Palshin, V.; Meletis, E.I. Structure-property relationship of Si-DLC films. *Surf. Coat. Technol.* **2001**, *148*, 305–314.
18. Baba, K.; Hatada, R. Deposition and characterization of Ti- and W-containing diamond-like carbon films by plasma source ion implantation. *Surf. Coat. Technol.* **2003**, *169*, 287–290.
19. Liu, C.; Li, G.; Chen, W.; Mu, Z.; Zhang, C.; Wang, L. The study of doped DLC films by Ti ion implantation. *Thin Solid Films* **2005**, *475*, 279–282.
20. Ouyang, J.H.; Sasaki, S.; Friction and wear characteristics of a Ti-containing diamond-like carbon coating with an SRV tester high contact load and elevated temperature. *Surf. Coat. Technol.* **2005**, *195*, 234–244.
21. Iseki, T.; Mori, H.; Hasegawa, H.; Tachikawa, H.; Nakanishi, K. Structural analysis of Si-containing diamond-like carbon. *Diam. Relat. Mater.* **2006**, *15*, 1004–1010.
22. Zhao, F.; Li, H.; Jo, L.; Wang, Y.; Zhou, H.; Chen, J. Ti-DLC films with superior friction performance. *Diam. Relat. Mater.* **2010**, *19*, 342–349.
23. Caschera, D.; Federici, F.; Pandolfi, L.; Kaciulis, S.; Sebastiani, M.; Bemporad, E.; Padeletti, G. Effect of composition on mechanical behaviour of diamond-like carbon coatings modified with titanium. *Thin Solid Films* **2011**, *519*, 3061–3067.

24. Hofmann, D.; Kunkel, S.; Bewilogua, K.; Wittorf, R. From DLC to Si-DLC layer systems with properties for tribological applications. *Surf. Coat. Technol.* **2013**, *215*, 357–363.
25. Amanov, A.; Watave, T.; Tsuboi, R.; Sakaki, S. Improvement in the tribological characteristics of Si-DLC coating by laser surface texturing under oil-lubricated point contacts at various temperatures. *Suf. Coat. Technol.* **2013**, *232*, 549–560.
26. Lubwama, M.; Corcoran, B.; McDonnell, K.A.; Dowling, D.; Kirabira, J.B.; Sebbit, A.; Sayers, K. Flexibility and frictional behaviour of DLC and Si-DLC films deposited on nitrile rubber. *Surf. Coat. Technol.* **2014**, *239*, 84–94.
27. Wang, S.; Wang, F.; Liao, Z.; Wang, Q.; Tyagi, R.; Liu, W. Tribological behaviour of titanium alloy modified by carbon–DLC composite film. *Surf. Eng.* **2015**, doi:10.1179/1743294414Y.00000000452
28. Kanda, K.; Fukuda, K.; Kidena, K.; Imai, R.; Niibe, M.; Fujimoto, S.; Yokota, K.; Tagawa, M. Hyperthermal atomic oxygen beam irradiation effect on the Ti-containing DLC film. *Diam. Relat. Mater.* **2014**, *41*, 49–52.
29. Nakahigashi, T.; Tanaka, Y.; Miyake, K.; Oohara, H. Properties of flexible DLC film deposited by amplitude-modulated RE P-CVD. *Triol. Int.* **2004**, *37*, 907–912.
30. Tagawa, M.; Yokota, K.; Ohmae, N.; Kinoshita, H.; Umeno, M. Oxidation Properties of Hydrogen-Terminated Si(001) Surfaces Following Use of a Hyperthermal Broad Atomic Oxygen Beam at Low Temperatures. *Jpn. J. Appl. Phys.* **2001**, *40*, 6152–6156.
31. Yokota, K.; Tagawa, M.; Ohmae, N. Temperature Dependence in Erosion Rates of Polyimide under Hyerthermal Atomic Oxygen Exposures. *J. Spacecr. Rockets* **2003**, *40*, 143.
32. Kitamura, A.; Tamai, T.; Taniike, A.; Furuyama, Y.; Maeda, T.; Ogiwara, N.; Saidoh, M. Simulation of ERD spectra for a surface with a periodic roughness. *Nucl. Instrum. Methods Phys. Res. Sect. B* **1998**, *134*, 98–106.
33. Niibe, M.; Mukai, M.; Miyamoto, S.; Shoji, Y.; Hashimoto, S.; Ando, A.; Tanaka, T.; Miyai, M.; Kitamura, H. Characterization of light radiated from 11 m long undulator. *AIP Conf. Proc.* **2004**, *705*, 576–579.
34. Niibe, M.; Mukai, M.; Kimura, H.; Shoji, Y. Polarization property measurement of the long undulator radiation using Cr/C multilayer polarization elements. *AIP Conf. Proc.* **2004**, *705*, 243–246.
35. Saikubo, A.; Kanda, K.; Niibe, M.; Matsui, S. Near-edge X-ray absorption fine-structure characterization of diamond-like-carbon thin films formed by various method. *New Diam. Front. Carbon Technol.* **2006**, *16*, 235–244.
36. Saikubo, A.; Yamada, N.; Kanda, K.; Matsui, S.; Suzuki, T.; Niihara, K.; Saitoh, H. Comprehensive classification of DLC films formed by various methods using NEXAFS measurement. *Diam. Relat. Mater.* **2008**, *17*, 1743–1745.
37. Nam, S.H.; Cho, S.J.; Jung, C.K.; Boo, J.H.; Šícha, J.; Heřman, D.; Musil, J.; Vlček, J. Comparison of hydrophilic properties of TiO<sub>2</sub> thin films prepared by sol-gel method and reactive magnetron sputtering system. *Thin Solid Films* **2011**, *519*, 6944–6950.
38. Kanda, K.; Niibe, M.; Wada, A.; Ito, H.; Suzuki, T.; Ohana, T.; Ohtake, N.; Saitoh, H. Comprehensive Classification of Near-Edge X-ray Absorption Fine Structure Spectra of Si-Containing Diamond-Like Carbon thin Films. *Jpn. J. Appl. Phys.* **2013**, *52*, 095504.

39. Magnuson, M.; Lewin, E.; Hultman, L.; Jansson, U. Electronic structure and chemical bonding of nanocrystalline-TiC/amorphous-C nanocomposites. *Phys. Rev. B* **2009**, *80*, 235108.
40. Kucheyev, S.O.; Buuren, T.V.; Baumann, T.F.; Satcher, J.H., Jr.; Willey, T.M.; Meulenberg, R.W.; Felter, T.E.; Poco, J.F.; Gammon, S.A.; Terminello, L.J. Electronic structure of titania aerogels: Soft X-ray absorption study. *Phys. Rev. B* **2004**, *69*, 245102.
41. Tagawa, M.; Yokota, K.; Ochi, K.; Akiyama, M.; Matsumoto, K.; Suzuki, M. Comparison of Macro and Microtribological Property of Molybdenum Disulfide Film Exposed to LEO Space Environment. *Tribol. Lett.* **2012**, *45*, 349–356.

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