



# Hyperthermal atomic oxygen beam irradiation effect on the Ti-containing DLC film<sup>☆</sup>



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## ABSTRACT

Surface structural changes of Ti-doped diamond-like carbon (Ti-DLC) film exposed to a hyperthermal atomic oxygen beam were investigated using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy using synchrotron radiation. The spectral shape of the C K NEXAFS spectrum of as-deposited Ti-DLC film resembled that of DLC film. After exposure to atomic oxygen, the spectrum resembled that of TiC powder. The  $sp^2/(sp^2 + sp^3)$  ratio of as-deposited Ti-DLC film decreased drastically by exposure to a hyperthermal atomic oxygen beam. On the other hand, the spectral shape in the Ti L NEXAFS spectrum of as-deposited Ti-DLC film resembled that of TiC powder and became similar to that of TiO<sub>2</sub> powder after exposure to atomic oxygen. These changes are ascribable to the desorption of C atoms as CO and/or CO<sub>2</sub> from Ti-DLC film due to the irradiation of atomic oxygen beam. On the other hand, oxidized Ti was not desorbed from the Ti-DLC film. As a result, the  $sp^2/(sp^2 + sp^3)$  ratio of C in the Ti-DLC film decreased, because residual C atoms were bonded to Ti atoms.

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## 1. Introduction

Diamond-like carbon (DLC) films have been used as coating material on edged tools, molds, computer hard disks, optical devices, food containers, and as an implantation material to a living body, because they have a wide range of properties including low friction coefficient, high hardness, high wear and corrosion resistance, chemical inertness, high electrical resistivity, infrared transparency, high refractive index, and excellent smoothness [1–5]. DLC films are known to exhibit a low friction coefficient as well as a low wear rate in ambient air and water environments; however, their friction coefficient is too high for lubrication applications in a vacuum. In 1994, Donnet et al. reported that DLC films with a hydrogen content greater than 40 at.% provide ultra-low friction (friction coefficient less than 0.001), even under vacuum conditions [6]. After this report, DLC films were expected to be used as lubrication materials in space, where oil cannot be used, because they exhibit excellent friction properties both in a vacuum and in air.

One of the most important concerns is the reliability of DLC films as a lubricating material in an extreme space environment (temperature, soft X-ray, radiation of atomic oxygen, and their synergistic conditions). DLC films having large amounts of hydrogen were reported modified by the exposure to synchrotron radiation (SR) in the soft X-ray region [7]. The

most important factor in causing deterioration of the material in low Earth orbit (LEO), where artificial satellites and spacecraft are positioned, is atomic oxygen exposure. In this orbit, artificial satellites and spacecraft are exposed to atomic oxygen with the translation energy of 5 eV [8]. In our previous study, we investigated the effects of atomic oxygen exposure with an impinging energy of 5 eV on the surface chemistry and structure of DLC film surfaces by using an atomic oxygen beam source. A departure of hydrogen from DLC films and structural change of carbon atom in the surface layer of a hydrogenated DLC film were verified during hyperthermal atomic oxygen exposure [9,10].

Recently, the development of functional DLC films advanced due to the incorporation of other elements, such as N, Si, F, and metal content, into DLC films to enhance their electrical, optical, and mechanical properties [11–16]. In particular, Ti-doped DLC films have been widely investigated due to their thermal stability [17–24]. In the present study, we investigated the effect of atomic oxygen exposure with an impinging energy of 5 eV on the surface chemistry and structure of Ti-DLC films by measuring the near-edge X-ray absorption fine structure (NEXAFS) spectra. The NEXAFS spectroscopy using synchrotron radiation is sensitive to the local structure of amorphous C thin films [25–27]. Specifically C K-edge NEXAFS spectroscopy has been used as an efficient method of determining the  $sp^2$  content of DLC films [28–30].

## 2. Experimental methods

The Ti-containing hydrogenated DLC (Ti-DLC) films used in this study are commercially available (Nippon ITF). The films were deposited at 200 nm thickness on Si wafers using CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> gases by using an

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amplitude modulated RF plasma-enhanced chemical vapor deposition (CVD) method [31]. The hydrogen content of these films were estimated to be greater than 40 at.% using the combination of Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) of DLC films by using the same synthesis method [7].

The exposure of an atomic oxygen beam into the Ti-DLC films was done using a laser detonation-type beam apparatus [10,32–34]. Pure oxygen gas is introduced into the nozzle throat through a pulsed supersonic valve. A pulse from a CO<sub>2</sub> laser (10.6 μm, >5 J/pulse) is focused into the oxygen gas at the nozzle throat. By absorbing the laser energy, high-density and high-temperature oxygen plasma is formed at the nozzle throat. Once the plasma is formed, it propagates and absorbs the energy in the tail of the laser pulse. This plasma propagation occurs along at the incident laser axis, and oxygen molecules are decomposed and accelerated at the shock front of the plasma propagation. The translational energy of 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. 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 Ag-coated quartz crystal microbalance (QCM). In the present study, four sheets of Ti-DLC film were exposed to an atomic oxygen beam corresponding to the fluences of  $2.74 \times 10^{19}$ ,  $5.47 \times 10^{19}$ ,  $8.3 \times 10^{19}$ , and  $1.85 \times 10^{20}$  atoms cm<sup>-2</sup>, respectively. All exposure experiments were carried out at room temperature.

Elementary analysis of the Ti-DLC film surfaces was conducted by measuring the X-ray photoelectron spectra (XPS), which was carried out using a conventional photoelectron spectroscopy apparatus (Shimadzu ESCA-1000) mounted with a CL150 (VSW Ltd.) hemispherical electron energy analyzer. The Mg Kα line ( $h\nu = 1253.6$  eV), used as the X-ray source, was incident at 45° with respect to the emission angle of 45° to the surface normal.

The NEXAFS measurements were carried out on beamline 09A (BL09A) at the New SUBARU synchrotron radiation facility, which has a 1.5-GeV electron storage ring [35,36]. Synchrotron radiation emitted by an 11-m undulator was extracted using a varied line spacing plane grating with 1200 lines/mm and irradiated on the sample film at the “magic angle” of 54.7° with respect to the surface normal. 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 and Ti L edge absorption were measured in the range 275–330 eV and 450–500 eV, respectively.

### 3. Results and discussion

Variation in the elementary composition of the Ti-DLC films due to the irradiation of an atomic oxygen beam was analyzed from the XPS spectra. Fig. 1 shows the XPS spectra of the Ti-DLC films before and after exposure to an atomic oxygen beam of  $2.74 \times 10^{19}$  and  $5.47 \times 10^{19}$  atoms cm<sup>-2</sup>. Several peaks originating from C, Ti, and O atoms, were observed in the spectrum of the Ti-DLC film before exposure. The peaks at 532, 458, and 285 eV were assigned to the O1s, Ti 2p, and C1s, respectively. The O atoms can be regarded as absorbed atoms on the Ti-DLC film surface. The intensity of the peak originating from Ti was weak.

After exposure to an atomic oxygen beam, the intensity of the peaks originating from the Ti and O atoms increased and those originating from the C atoms decreased. The results of elementary analysis are listed in Table 1. The amount of O atoms in the Ti-DLC films increased with the fluence of the atomic oxygen beam. However, that of C atoms decreased monotonically. The percentage of Ti atoms increased after exposure to

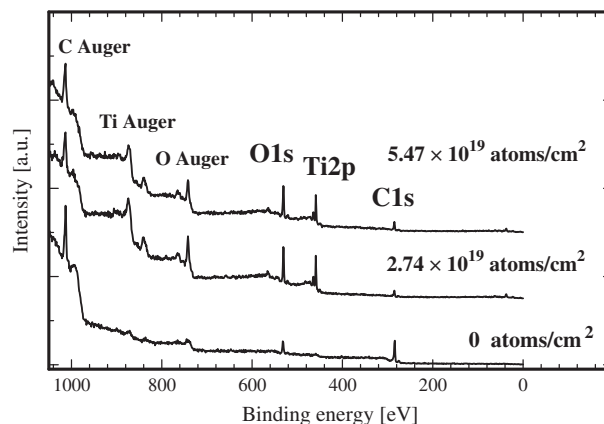


Fig. 1. XPS spectra of Ti-DLC films before and after exposure to atomic oxygen beam of  $2.74 \times 10^{19}$  and  $5.47 \times 10^{19}$  atoms cm<sup>-2</sup>.

an atomic oxygen beam of  $2.74 \times 10^{19}$  atoms cm<sup>-2</sup> and decreased after exposure to an atomic oxygen beam of  $5.47 \times 10^{19}$  atoms cm<sup>-2</sup> due to the increase in the O percentage.

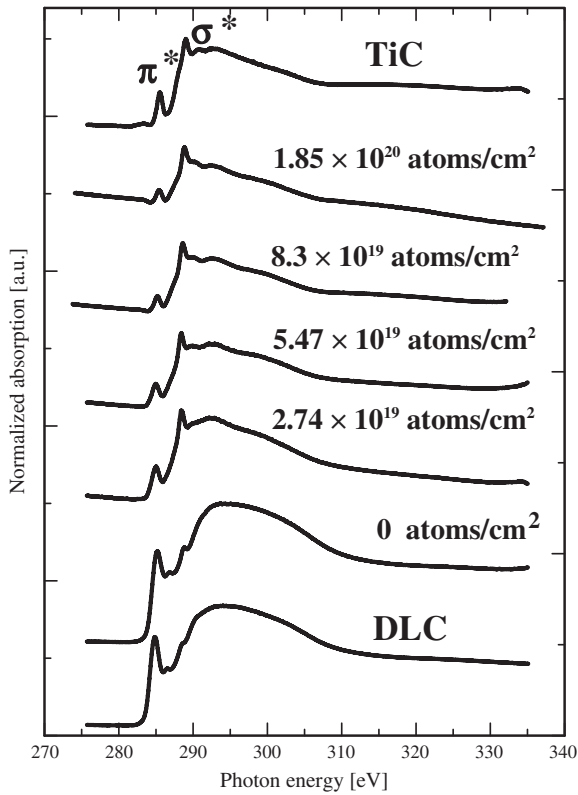
Variations in the local structure of the Ti-DLC film due to the exposure to an atomic oxygen beam are discussed on the basis of the NEXAFS measurements. Fig. 2 shows the C K-edge NEXAFS spectra of a Ti-DLC film exposed to by an atomic oxygen beam with that of a Ti-DLC film before exposure. The spectra of a commercial DLC film without Ti by using the ion-plating method and TiC powder are also shown for reference. A pre-edge resonance at 285.4 eV was due to transitions from the C 1s level to unoccupied  $\pi^*$  orbitals principally originating from  $sp^2$  (C = C) sites. The transitions from C 1s level to unoccupied  $\sigma^*$  states were observed in the photon energy region of 290–320 eV. The spectral features of the C K NEXAFS spectrum of the Ti-DLC film before exposure resembled that of the DLC film. In other words, the local structure of the C in the Ti-DLC films used in this study is close to that in the DLC film without Ti. A small shoulder peak was observed at 289 eV.

The spectral features of the C K NEXAFS spectrum of the Ti-DLC film noticeably changed the exposure to an atomic oxygen beam. 1) A sharp peak was observed at 289 eV due to the increase in intensity at which a peak was observed as a small shoulder peak in the spectrum of the Ti-DLC film before exposure. 2) The intensity of the peak at 285.4 eV decreased. This decrease indicates that the  $sp^2$  component decreased in the Ti-DLC film. The spectral features of the Ti-DLC film after exposure to atomic oxygen beam resembled that of TiC powder. In other words, a large percentage of the C atoms in the Ti-DLC films coupled with Ti atoms due to the exposure to an atomic oxygen beam. In addition, the peak at 289 eV was assignable to the 1s  $\rightarrow \sigma^*$  transition originating from the C atoms neighboring the Ti atoms.

It is known that the  $sp^2$  content obtained from C K NEXAFS spectra is a good index for DLC properties, and NEXAFS spectroscopy is a suitable method for evaluating DLC films. A method of determining the  $sp^2$  content from NEXAFS spectrum was described in ref. [28–30]. In the present study, the absolute value of the  $sp^2/(sp^2 + sp^3)$  ratio was estimated by comparing it with that of graphite. The error range of the determined  $sp^2/(sp^2 + sp^3)$  ratio was estimated to be less than 10%.

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

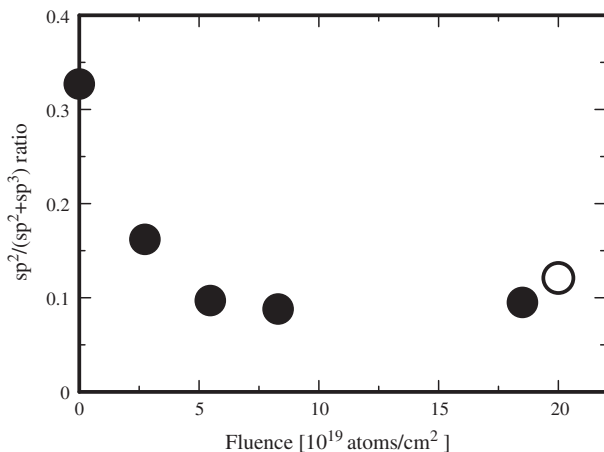
Fluence atoms cm <sup>-2</sup>	C	O at.%	Ti
0	40	25	36
$2.74 \times 10^{19}$	12	43	45
$5.47 \times 10^{19}$	9	63	28



**Fig. 2.** C K-edge NEXAFS spectra of commercial DLC film and Ti-DLC films before and after exposure to atomic oxygen beam and TiC powder.

The dependence of the  $sp^2/(sp^2 + sp^3)$  ratio on the fluence of the atomic oxygen beam is plotted in Fig. 3. The  $sp^2/(sp^2 + sp^3)$  ratio of as-deposited Ti-DLC films was  $\approx 0.33$ . After exposure to an atomic oxygen beam of  $2.74 \times 10^{19}$  atoms  $cm^{-2}$ , the  $sp^2/(sp^2 + sp^3)$  ratio decreased to  $\approx 0.16$ . In other words, the  $sp^2/(sp^2 + sp^3)$  ratio exponentially decreased with increase in the fluence of the atomic oxygen beam and became close to that of TiC powder. This dependency on the  $sp^2/(sp^2 + sp^3)$  ratio of the C atoms in the Ti-DLC films did not agree with that in the DLC film, which did not contain any hetero-atoms, in which the  $sp^2/(sp^2 + sp^3)$  ratio was almost the same [10].

Fig. 4 shows the Ti L-edge NEXAFS spectra of the Ti-DLC exposed to an atomic oxygen beam with that of the Ti-DLC film before exposure. The spectra of the TiC powder and TiO<sub>2</sub> (rutile) powder are also



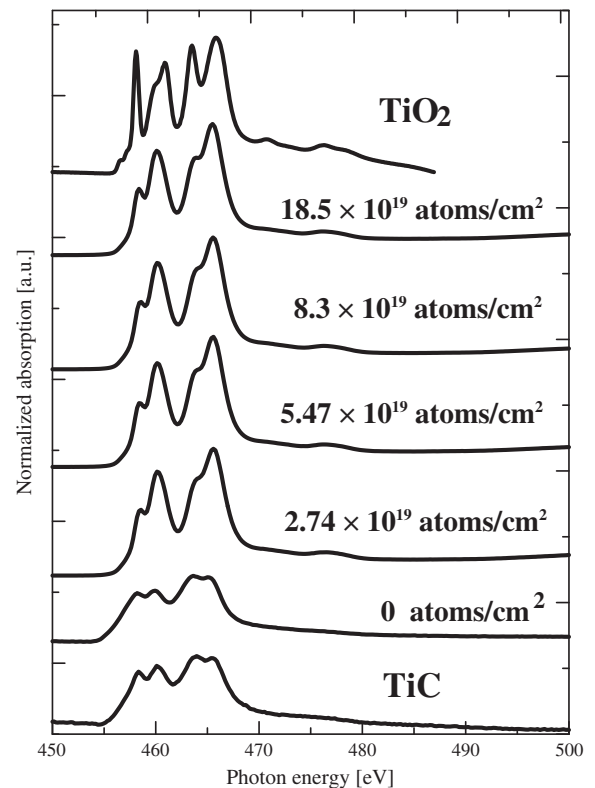
**Fig. 3.** Dependence of  $sp^2/(sp^2 + sp^3)$  ratio of C atoms in Ti-DLC films on fluence of atomic oxygen beam. Open circle indicates  $sp^2/(sp^2 + sp^3)$  ratio of TiC powder.

shown for reference. The spectral features of the Ti L NEXAFS spectrum of the Ti-DLC film before exposure resembled that of TiC powder. Therefore, a large percentage of the Ti atoms in the Ti-DLC films in the present study bonded with the C atoms. After exposure to an atomic oxygen beam, the spectral features of the Ti-DLC films changed and became similar to those of TiO<sub>2</sub> powder. In other words, most of the Ti atoms in the Ti-DLC films bonded with O atoms due to exposure to the atomic oxygen beam.

From the above XPS and NEXAFS results, the changes in the local structure of the Ti-DLC film due to exposure to an atomic oxygen beam are summarized as follows: 1) In the as-deposited Ti-DLC films, almost all the C atoms were bonded to each other with single bonding and double bonding at a certain ratio. Most of the Ti atoms bonded to the C atoms. 2) After exposure to an atomic oxygen beam, most of the C atoms bonded to Ti atoms and most of the Ti atoms bonded to the O atoms. These changes are ascribable to desorption of C atoms from Ti-DLC films due to the irradiation of the atomic oxygen beam. The C atoms were desorbed from the films as gas species (CO and/or CO<sub>2</sub>). On the other hand, oxidized Ti (TiO<sub>x</sub>) was not desorbed from the Ti-DLC films as a gas species. Therefore, the Ti/C ratio on the surface of the Ti-DLC films increased due to the irradiation of the atomic oxygen beam. As the result, residual C atoms bonded to the Ti atoms. The  $sp^2/(sp^2 + sp^3)$  ratio of C atoms in the Ti-DLC films exponentially decreased because the C-Ti bonding could not form double bonding. The discrepancy at the previous work on DLC film [10] is ascribable to Ti-DLC films containing Ti atoms, which were not desorbed from the film even if they were oxidized due to the irradiation of an atomic oxygen beam.

#### 4. Conclusion

Surface structural changes of a Ti-doped diamond-like carbon (Ti-DLC) film exposed to a hyperthermal atomic oxygen beam were



**Fig. 4.** Ti L-edge NEXAFS spectra of TiC powder, Ti-DLC films before and after exposure to atomic oxygen, and TiO<sub>2</sub> powder.

investigated by near-edge X-ray absorption fine structure (NEXAFS). It was confirmed that the C atoms on the Ti-DLC surface were desorbed as the CO and/or CO<sub>2</sub> and Ti atoms were remained on the Ti-DLC surface as the TiO<sub>x</sub>. NEXAFS data suggested that the sp<sup>2</sup> structure at the Ti-DLC surface was decreased, because the content of C atoms decreased and the residual C atoms were necessarily bonded to Ti atoms. We are planning to measure the Raman spectra, hardness, friction coefficient, and corrosion resistance to put the Ti-DLC films on a scale and to practical use in the LEO.

### Prime novelty statement

This is the first report on exposure of Ti-doped diamond-like carbon (Ti-DLC) films to a hyperthermal atomic oxygen beam. The deterioration mechanism that became clear by this work is important for the application of Ti-DLC films into astronautics items.

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