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Soft X-ray irradiation effect on the surface and material properties of highly hydrogenated diamond-like carbon thin films ☆

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ABSTRACT

Surface and bulk properties' changes of a hydrogenated diamond-like carbon (H-DLC) film exposed to synchrotron radiation (SR) in the soft X-ray region were investigated by a nano-indenter, an atomic force microscope (AFM), and a combination of Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA) techniques. The surface of H-DLC films became flat and the hydrogen content of H-DLC films decreased with increasing SR dose. On the other hand, Vickers hardness showed the complicated dependency on the SR dose. It was found that modification processes of H-DLC films by SR exposure included three reactions: flattening on the surface, hydrogen desorption, and etching by SR exposure.

1. Introduction

Diamond-like carbon (DLC) films have excellent properties including high hardness, a low friction coefficient, high abrasion quality, a gas barrier, chemical inertness, and surface lubrication and are therefore being utilized as coating materials on automobile parts, hard disks, artificial blood vessels, edged tools, and food containers. Film-forming methods affect the properties of DLC films differently, and thus a wide variety of DLC films have been developed. DLC films are expected to be used in outer space as a lubrication substitution for oil [1,2], which cannot be used in space because it disappears in vacuums [3].

DLC films, which are amorphous, contain sp^2 hybridized carbon corresponding to a graphite structure and sp^3 hybridized carbon corresponding to a diamond structure. DLC films include a certain amount of hydrogen, generally from 20% to 30%, and have free space inside the films due to their amorphous structure. The sp^2/sp^3 ratio and hydrogen content have been widely recognized as the structural parameters that characterize DLC film properties [4]. Ternary phase diagram on the relation between the sp^2/sp^3 ratio and the hydrogen content has been propounded by Jacob and Möller [5], and Ferrari and Robertson [6].

DLC films are generally durable against X-ray exposure [7]. However, it has recently been reported that soft X-ray exposure on highly hydrogenated DLC (H-DLC) films leads to desorption of hydrogen and an increase in film density and refractive index [8,9]. A theoretical calculation has suggested that this hydrogen desorption could be associated with a structural change of DLC films [10]. Clarification of the effect of soft X-ray exposure on DLC films is necessary to ensure that DLC films can be used in outer space safely.

In a previous study, soft X-ray exposure on H-DLC films, which contain hydrogen over ≈40%, was found to lead to hydrogen desorption and etching of films proportional to synchrotron radiation (SR) irradiation dose [8]. The thermal durability of H-DLC films has also been investigated [11]. Still, the modification effect of soft X-ray exposure on H-DLC films is not yet fully understood.

In this study, we investigated the modification processes by soft X-ray exposure on H-DLC films. Specifically the SR dose dependence of Vickers hardness, surface roughness, and hydrogen content was investigated. The Vickers hardness was measured using a nanoindenter. The elementary composition analysis was performed using a combination of Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA) techniques. The surface roughness was measured using an atomic force microscope (AFM).

2. Material and methods

200-nm-thick H-DLC films were deposited on Si wafers by using an amplitude-modulated RF plasma-enhanced CVD method [12,13]. This

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method enables the deposition of DLC films containing a lot of hydrogen. The SR irradiation of the H-DLC films was carried out at BL06 of the NewSUBARU synchrotron facility at the University of Hyogo, Japan [13]. Detailed information on BL06 was reported on ref. [14] and [15]. The SR at the BL06 sample stage had a continuous spectrum from IR to soft X-rays, lower than 1 keV. This includes 300 eV, which is the ionization energy of a carbon *K* edge. As a result, the *K*-shell electrons of the C atoms were excited by the SR at BL06. Inner shell excitation of the C atoms caused by irradiation with 300 eV changes chemical environment in DLC films and enables surface modification of DLC films. During this experiment, the electron energy of the NewSUBARU ring was 1.0 GeV. The luminance of SR at BL06 when electron energy of it is 1.0 GeV is about three hundred times intensity at 10 eV compared with irradiation in revolution orbit of the Earth from the sun, and the difference in luminance between them will widen with increasing photon energy. The detail on the luminance of BL06 was described in ref. [16]. Therefore the present experiment corresponds to acceleration test. The BL06 sample stage was room temperature and the pressure in the chamber was the order of 10^{-5} Pa. An SR dose [mA·h] is derived from the product of the ring current [mA] and exposure time [h]. The exposure on the H-DLC films was carried out over SR doses ranging from 0 to 3000 mA·h.

3. Results and discussion

The hydrogen content of H-DLC films was quantitatively determined by RBS/ERDA. The measurements were performed using an electrostatic accelerator (Nissin High Voltage, NT-1700HS) located at the Extreme Energy-Density Research Institute, Nagaoka University of Technology, Japan. He^+ ions accelerated to 2.5 MeV using a tandem Pelletron accelerator were used as the incident beam, whose angle with respect to the surface normal was 72°. The measurement error of this apparatus is 1%. The experimental apparatus of RBS/ERDA is described in detail in [17–20].

Fig. 1 shows the SR dose dependence of the hydrogen content of H-DLC films. The hydrogen content of the unirradiated H-DLC films was ≈50%. After SR exposure, the hydrogen content drastically decreased in the range of 0–200 mA·h, eventually becoming ≈30% at 200 mA·h. Above ≈200 mA·h, the hydrogen content slowly decreased and consequently became ≈20%. This result shows that the SR exposure on H-DLC films leads to hydrogen desorption. However, hydrogen of ≈20% in H-DLC films was not affected due to SR exposure. This indicates that hydrogen atoms exist at different chemical environments in H-DLC films: first is the hydrogen emitted from by the exposure to soft X-rays and second is the hydrogen not emitted. It has previously been found that the structure of H-DLC films varied to that of typical DLC films whose hydrogen content is 20–30% by the exposure to soft X-rays [8].

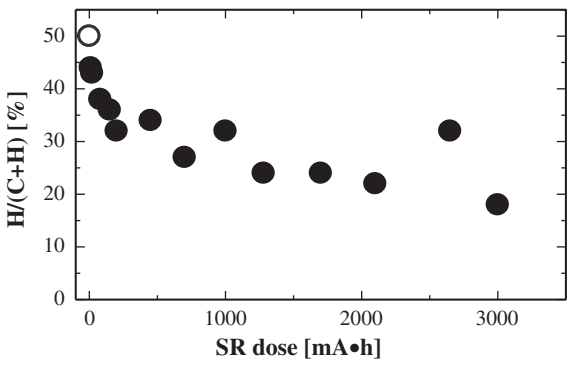

Fig. 1. SR dose dependence of hydrogen content of H-DLC films. ○ and ● represent unirradiated and irradiated, respectively.

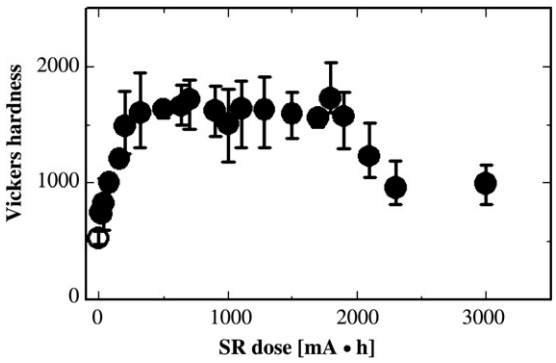

Fig. 2. SR dose dependence of hydrogen content of H-DLC films. ○ and ● represent unirradiated and irradiated, respectively.

Fig. 2 shows the SR dose dependence of Vickers hardness. We measured the Vickers hardness of H-DLC films using a nanoindenter (ELIONIX NT-110a). In this measurement, the sample surface was pressed to ≈20 nm, which was a tenth of the film's thickness (200 nm), using a quadrilateral diamond as the indenter. The average value in each sample is plotted in Fig. 2. The Vickers hardness of the unirradiated H-DLC films was ≈500 HV. After the SR exposure, it steeply increased in the range of 0–200 mA·h, eventually becoming ≈1600 HV at 200 mA·h. Above ≈200 mA·h, it remained approximately constant at ≈1600 HV. It slowly decreased above ≈2000 mA·h and remained at ≈1000 HV above ≈2300 mA·h.

As shown Figs. 1 and 2, a rapid reaction in the range of ≈0–200 mA·h was observed in the hydrogen content and Vickers hardness. In this SR dose region, it has been shown that hydrogen desorption by SR exposure leads to the graphitization of DLC films: the C – H bond decouples and the C═C bond couples [11,21–23]. This is considered to increase the hardness of H-DLC films because of the hydrogen desorption in the films. In the range of 200–1600 mA·h, hydrogen desorption as above was not observed but rather remained constant at ≈30%. Vickers hardness also remained constant at ≈1600 HV. In this SR dose region, it appears that SR exposure on the H-DLC films slowly leads to desorption of carbon and hydrogen and to the etching of the films. In the range of 1600–2300 mA·h, the Vickers hardness decreased to ≈1000 HV, and it remained constant at ≈1000 HV above ≈2300 mA·h. This tendency is ascribable to the thickness of H-DLC films decreased by the etching and measured hardness was affected by the substrate Si wafer, whose Vickers hardness was ≈1200 HV.

The surface roughness (Ra) and the peak-to-valley value (P–V) of the H-DLC films were measured by using a tapping method with AFM apparatus (SII Nanotechnology E-sweep/NanoNavi Station); the determining area was 1000 × 1000 nm. SR dose dependence of Ra and P–V estimated by the measurements of AFM, is shown in Figs. 3 and 4,

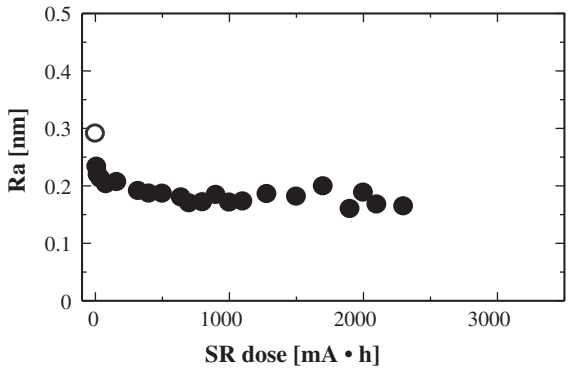

Fig. 3. SR dose dependence of Vickers hardness of H-DLC films. ○ and ● represent unirradiated and irradiated, respectively.

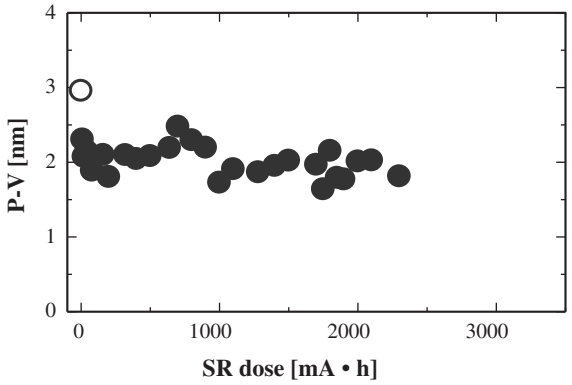

Fig. 4. SR dose dependence of surface roughness of H-DLC films. ○ and ● represent unirradiated and irradiated, respectively.

respectively. The Ra of the unirradiated H-DLC films was 0.29 nm, which was the largest. The Ra of H-DLC films with even the smallest SR dose (10 mA·h) rapidly decreased compared to the unirradiated one. In addition, Ra remained approximately constant at ≈0.18 nm in regions above ≈100 mA·h. The P–V of unirradiated H-DLC films also decreased rapidly by SR exposure. These results show that SR exposure on H-DLC films led to a decrease of both Ra and P–V, and it also flattened the surface of the H-DLC films. In terms of the Vickers hardness and hydrogen content, the change was observed in ≈0–200 mA·h. In contrast, the process of flattening decreased at a lower SR dose. Therefore, the process of surface flattening differs from that of hydrogen desorption.

The modification of H-DLC films by the SR exposure includes three reaction processes: surface flattening, hydrogen desorption, and etching of the surface. Immediately after the SR exposure, the surface becomes flat due to desorption from the salient. Up to ≈200 mA·h, the hydrogen content of the H-DLC films was ≈30% and the Vickers hardness was ≈1600 HV. In SR dose ≈200 mA·h and over, the H-DLC films were etched by the SR exposure.

4. Conclusions

Soft X-ray irradiation effect on the surface and material properties of highly hydrogenated diamond-like carbon thin films was investigated using a nano-indenter, an atomic force microscope (AFM), and a combination of Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA) techniques. The exposure to the SR, which includes the ionization energy 300 eV, excites the inner shell of a carbon *K* edge in this experiment. This inner shell excitation breaks chemical bonds of DLC films and then the surface modification of DLC films was carried out. This modification caused to decrease hydrogen content the roughness and to increase hardness.

The hydrogen content of H-DLC films decreased from ≈50% to ≈20% by the SR exposure on films. Hydrogen desorption was not observed at higher doses. The Vickers hardness of the films was found to increase from ≈500 HV to ≈1600 HV. The dose dependence of the hydrogen content was similar to that of the Vickers hardness. In the range of ≈0–200 mA·h, hydrogen content decreased and Vickers hardness increased steeply. In contrast, the surface roughness and P–V of the H-DLC films decreased at lower SR doses, which was different from other hydrogen content and Vickers hardness. As a result, the surface of the H-DLC films became flat. We found that the modification processes of H-DLC films by SR exposure include three reactions: flattening on the surface, hydrogen desorption, and etching.

Prime novelty statement

The process on the exposure of highly hydrogenated diamond-like carbon to soft X-ray was discussed from the AFM, nano-indenter, and ERDA studies.

We found that three competitive reactions are included in this process.

References

[1] C. Donnet, J. Fontaine, T. Le mogne, M. Belin, C. Héau, J.P. Terrat, F. Vaux, G. Pont, Diamond-like carbon-based functionally gradient coatings for space tribology, Surf. Coat. Technol. 120 (1999) 548.
[2] C. Donnet, A. Erdemir, Diamond-like Carbon Films: A Historical Overview, Tribology of Diamond-like Carbon, Springer, 2008.
[3] C. Donnet, M. Belin, J.C. Augé, J.M. Martin, A. Grill, V. Patel, Tribochemistry of diamond-like carbon coatings in various environments, Surf. Coat. Technol. 68/69 (1994) 626.
[4] J. Robertson, Diamond-like amorphous carbon, Mate. Sci. Eng. R 37 (2002) 129.
[5] W. Jacob, W. Möller, On the structure of thin hydrocarbon films, Appl. Phys. Lett. 63 (1993) 1771.
[6] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B61 (2000) 14095.
[7] H. Kyuragi, T. Urisu, Synchrotron radiation-induced etching of a carbon film in an oxygen gas, Appl. Phys. Lett. 50 (1987) 1254.
[8] K. Kanda, K. Yokota, M. Tagawa, M. Tode, Y. Teraoka, S. Matsui, Effect of the soft X-rays on highly hydrogenated diamond-like carbon films, Jpn. J. Appl. Phys. 50 (2011) 055801.
[9] H. Matsuura, S. Ohkubo, K. Oda, T. Ushiro, Development of refractive-index modulation type diffractive optical element using a-C:H film, SEI, Tech. Rev. 171 (2007) 36 (in Japanese).
[10] Y. Miura, H. Kasai, W.A. Dinom, H. Nakanishi, T. Sugimoto, First principles studies for the dissociative adsorption of H_2 on graphene, J. Appl. Phys. 93 (2003) 3395.
[11] A. Fujimoto, M. Okada, Y. Kang, M. Niibe, S. Matsui, T. Suzuki, K. Kanda, Thermal durability of diamond like carbon films containing tungsten fabricated by focused-ion-beam chemical vapor deposition, Jpn. J. Appl. Phys. 51 (2012) 06FD07.
[12] T. Nakahigashi, Y. Tanaka, K. Miyake, H. Oohara, Properties of flexible DLC film deposited by amplitude-modulated RF P-CVD, Tribol. Int. 37 (2004) 907.
[13] A. Ando, S. Amano, S. Hashimoto, H. Kinoshita, S. Miyamoto, T. Mochizuki, M. Niibe, Y. Shoji, M. Terasawa, T. Watanabe, VUV and Soft X-ray Light Source "New SUBARU", Proc. IEE Particle Accelerator Conf, 1997, p. 757.
[14] K. Kanda, T. Ideta, Y. Haruyama, H. Ishigaki, S. Matsui, Surface modification of fluorocarbon polymers by synchrotron radiation, Jpn. J. Appl. Phys. 42 (2003) 3983.
[15] Y. Kato, K. Kanda, Y. Haruyama, S. Matsui, Synchrotron radiation effect in the soft X-ray region on the surface properties of pyromellitic dianhydride-oxydianline polyimide, Jpn. J. Appl. Phys. 43 (2004) 3938.
[16] Y. Kawamoto, K. Kobayashi, R. Imai, K. Kanda, Comparison of photon flux of a BL06 with that of the sun, LASTI Annual Report, 13, 2011, p. 64.
[17] Y. Ohkawara, S. Ohshio, T. Suzuki, H. Ito, K. Yatsui, H. Saitoh, Quantitative analysis of hydrogen in amorphous films of hydrogenated carbon nitride, Jpn. J. Physiol. 40 (2001) 7007.
[18] Y. Ohkawara, S. Ohshio, T. Suzuki, H. Ito, K. Yatsui, H. Saitoh, Dehydrogenation of nitrogen-containing carbon films by high-energy He^{2+} irradiation, Jpn. J. Appl. Phys. 40 (2001) 3359.
[19] J. Igaki, A. Saikubo, R. Kometani, K. Kanda, T. Suzuki, K. Niihara, S. Matsui, Elementary analysis of diamond-like carbon film formed by focused-ion-beam chemical vapor deposition, Jpn. J. Appl. Phys. 46 (2007) 8003.
[20] K. Kanda, M. Okada, Y. Kang, M. Niibe, A. Wada, H. Ito, T. Suzuki, S. Matsui, Structural changes in diamond-like carbon films fabricated by Ga focused-ion-beam-assisted deposition caused by annealing, Jpn. J. Appl. Phys. 49 (2010) 06GH06.
[21] K. Kanda, T. Kitagawa, Y. Shimizugawa, Y. Haruyama, S. Matsui, M. Terasawa, H. Tsubakino, I. Yamada, T. Gejo, M. Kamada, Characterization of hard diamond-like carbon films formed by Ar gas cluster ion beam-assisted fullerene deposition, Jpn. J. Appl. Phys. 41 (2002) 4295.
[22] A. Saikubo, K. Kanda, M. Niibe, S. Matsui, T. Suzuki, Near-edge X-ray absorption fine-structure characterization of diamond-like carbon thin film formed by various methods, New Diamond Front. Carbon Technol. 16 (2006) 235.
[23] A. Saikubo, N. Yamada, K. Kanda, S. Matsui, T. Suzuki, K. Niihara, H. Saitoh, Comprehensive classification of DLC films formed by various methods using NEXAFS measurement, Diamond Relat. Mater. 17 (2008) 1743.