XPS SPECTRUM OF DLC THIN FILMS CHANGED BY ARGON ION SPUTTERING

[1]KENJI YAMADA, [2]TORU HARIGAI, [3]HIROFUMI TAKIKAWA

[1]National Institute of Technology, Ishikawa College, Tsubata Ishikawa, 929-0392, Japan
[2,3]Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi, 441-8580, Japan
E-mail: [1]kenji@ishikawa-nct.ac.jp, [2]harigai@ee.tut.ac.jp, [2]takikawa@ee.tut.ac.jp

Abstract - We have investigated the bonding state of Diamond-like carbon (DLC) films by X-ray photoelectron spectroscopy (XPS). Different types of the DLC films (tetrahedral amorphous Carbon: ta-c and amorphous Carbon: a-c) were prepared on silicon wafer using a T-shape filtered arc deposition system (T-FAD). As a result of performing argon ion etching in order to remove the oxide film on the DLC film, the main component of the XPS C 1s spectrum became sp^2 hybrid orbital. We have obtained experimental results that sp^3 hybrid orbitalis the main component of this ta-c samples by several evaluation methods. Therefore, repeating the low energy etching cycle, as a result of increasing the waveform separation method to 4 components, the sp^3 surface component were decreased by etching, and sp^2 bulk component strength was increased.

Keywords - Diamond-like carbon, XPS, ta-C, a-C.

I. INTRODUCTION

Diamond-like carbon (DLC) has been used as a dry coating in a wide range of industrial fields. In our group the DLC film manufacturing equipmentwere developed by T-shape filtered arc deposition system (T-FAD) [1]. Depending on the magnitude of the bias voltage applied to the sample substrate, we can prepare ta-C or a-C. When the ta-C thin film sample was subjected to argon ion etching, XPS C 1s spectra were showed that the main component was sp^2hybrid orbital. However, we have already found that the main component of the ta-C film is sp^3hybrid orbital by various evaluation methods [2]. Therefore, we aim to investigate the change of XPS spectra by repeating low-energy argon etching cycle on the DLC surface. In the waveform processing method of the spectrum obtained, a two-component evaluation method that separates into sp^3 bond and sp^2 bond is commonto discuss the DLC films [3]. In addition to this method, we also consider four components consists of sp^3 surface component, sp^2 surface component, sp^2 bulk component and sp^3 bulk component respectively [4,5].

II. EXPERIMENTAL

The DLC film manufacturing equipment employed an electrostatic droplet trap for collecting submicron-sized particles, produced a clean pure carbon plasma [1]. On the Si substrate (10 mm × 10 mm), ta-c was prepared to a thickness of 90 nm with a bias voltage of 100 V, and a-c was prepared to a thickness of 440 nm with a bias voltage of 1000 V. As even more necessary, ta–C/a–C sampleobtained by depositing thick 5 nm ta–c on thick 50 nm a–C on the Si substrate was prepared. It is expected that what is the effect of etching should appear in each waveform-separated component. XPS measurements were undertaken using a Kratos AXIS-ULTRA.This experimental apparatus is a UHV chamber (base pressure ~$2x10^{-8}$ Pa) which is equipped with a monochromatic Al Kα1486 eV X-ray source. The analysis was employed the concentric hemispherical analyzer (CHA). On the resolution of analysis, when the sample of silver was irradiated with monochromatic Al Kα, the Ag 3d 5/2 photoelectron peak had a FWHM of 0.48 eV or less and the sensitivity was 2,400 cps or more under the condition that the analysis diameter was 30 μm or less. As the experimental conditions, the X-ray source was monochromatic Al Kα, the current was 5 mA, the voltage was 15 kV, and the path energy was set to 10. To control charging of the samples, the charge neutralizer filament was used during all experiments. All samples were mounted on a sample bar with a carbon tape and measured in the same atmosphere.The etching cycle was repeated with Acceleration voltage 3.5 kV and etching time 3 minutes as one cycle.We used CasaXPS software for waveform processing of all XPS spectra. The background removal was performed from the binding energy 282 eV to 288 eV by the Shirley method. As a next step, the spectra were separated using the Doniach Sunjic (DS) function [6].When using the DS function for waveform separation, we need to set the values of the singularity index α and the convolution width n as parameters. We set the α value to 0.02 with reference to the literature value [4,5]. When this α value increases, asymmetry also expands. By using the Shirley method for background removal, the α value may be set small. On the other hand, if the n value is set small, the tail structure of the waveform becomes large, resulting in a fitting deviation. The n value can be set up to 499, we set it to 400 in our study.

III. RESULTS AND DISCUSSION

Fig. 1 (a-d) indicates a comparison of XPS C 1s

spectra of DLC films (ta-c and a-c) about cases with and without etching. The spectrum (a) without etching shows the characteristics of ta-C that the main component separated by three waveform including weak C-O structure by natural oxidation is sp^3 bond. Spectrum (b) with etching once does not contain C-O structure. This result was also confirmed in the XPS O 1s spectrum.Since the sp^2 component of the spectrum (b) is larger than that of the spectrum (a), it was found that the sp^3 component on the thin film surface was reduced by etching. Spectra (c) and (d) show the results of the XPS spectrum obtained by substituting the sample for a-C. In the case of the a-C thin film surface, the situation mainly composed of sp^2 did not change by etching.

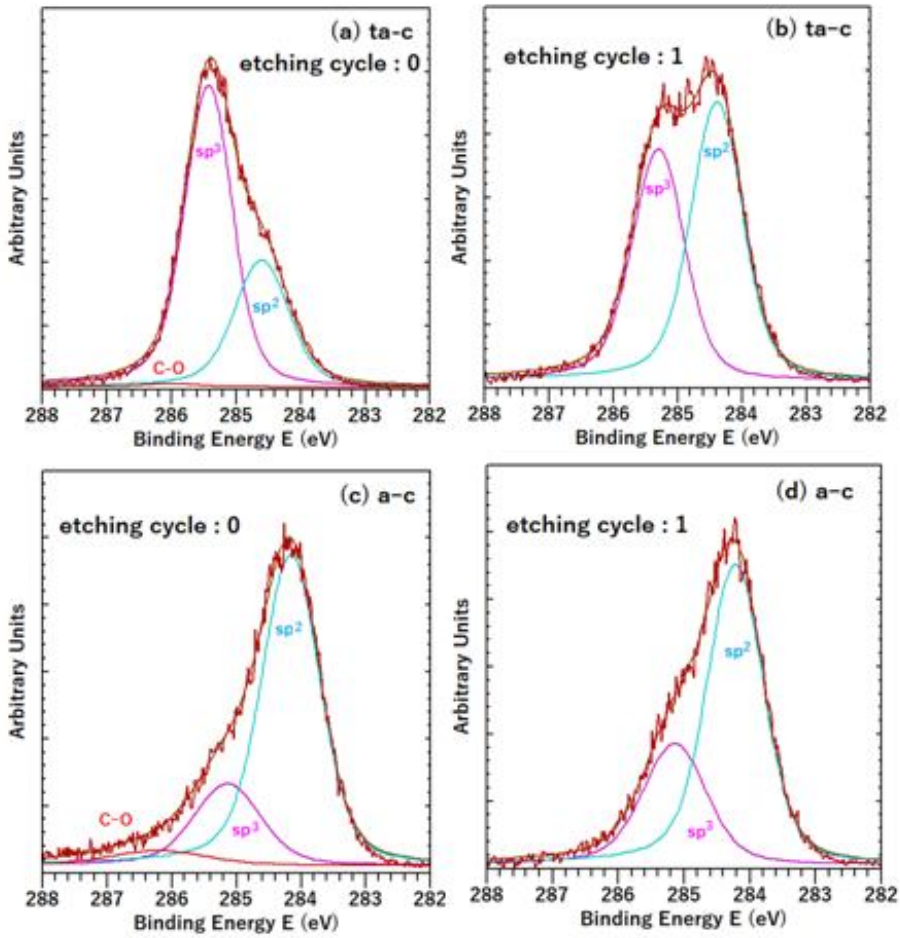

Fig. 1 Effect of etching on the components decomposed into two the XPS C1s spectra of DLC thin film.

(a) The spectra obtained from the ta-C without etching.
(b) The spectra obtained from the ta-C with etching once.
(c) The spectra obtained from the a-C without etching.
(d) The spectra obtained from the a-C with etching once.

The results of repeating the etching cycle are summarized in Table I as a data list. Data (1) is Binding energy (eV) of the peak position of where the waveform is separated. In order to confirm the deviation of each energy position, the difference from the value with sp^3 set to 285.2 eV and sp^2 set to 284.3 eV from the reference value [3] is shown in the table I as Δ. Although the Δ value without etching were a deviation of about 0.1 to 0.3 eV, after the etching is repeated, the deviation fallen within ± 0.1 eV.The full width at half maximum (FWHM) were about 1 eV as shown in data (2).Curve fitting becomes incompatible if the FWHM value is made small.Data (3) indicate atomic percent concentrationof the separate components.By repeating the etching cycle, sp^3 component decreased and sp^2 component increased.

Recently, the group of Takabayashi, et al. assigned the surface components and the bulk components to sp^3 bonds and sp^2 bonds respectively. They decomposed into four the components [3,4]. The separation results of the four components for the same data as in Fig 1. are shown in Fig 2. From high binding energy, it was able to separate as C-O, sp^3 surface component, sp^2 surface component, sp^2 bulk component, and sp^3 bulk component.From the waveform separation result of spectrum (a), it is found that the sp^3surface component

TABLE I. List of the XPS C1s data of the DLC films (ta-C and a-C) obtained by etching cycle. (1) Binding Energy Position [eV] and Difference Δ from standard value [eV], (2) FWHM: full width-half maximum [eV], (3) %At Conc : atomic percent of the deconvolution elements.

(1)E_B position eV		no etching	etching 1	etching 2	etching 3	etching 4
ta-c	sp^3	285.42	285.29	285.23	285.23	285.28
	sp^2	284.59	284.38	284.31	284.29	284.31
a-c	sp^3	285.13	285.13	285.18	285.18	
	sp^2	284.15	284.21	284.25	284.26	
ta-c	Δsp^3	0.22	0.09	0.03	0.03	0.08
	Δsp^2	0.29	0.08	0.01	-0.01	0.01
a-c	Δsp^3	-0.07	-0.07	-0.02	-0.02	
	Δsp^2	-0.15	-0.09	-0.05	-0.04	
(2)FWHM eV		no etching	etching 1	etching 2	etching 3	etching 4
ta-c	sp^3	0.86	0.96	1.06	1.08	0.94
	sp^2	0.99	0.95	0.94	0.98	1.01
a-c	sp^3	1.22	1.14	1.13	1.11	
	sp^2	1.06	1.01	1.02	1.00	
(3) %At Conc		no etching	etching 1	etching 2	etching 3	etching 4
ta-c	sp^3	66.81	45.57	42.52	38.19	29.49
	sp^2	32.20	54.43	57.48	61.81	70.51
	C-O	0.99	0.00	0.00	0.00	0.00
	Total	100	100	100	100	100
a-c	sp^3	21.93	31.28	31.58	30.87	
	sp^2	72.19	68.72	68.42	69.13	
	C-O	5.88	0.00	0.00	0.00	
	Total	100	100	100	100	

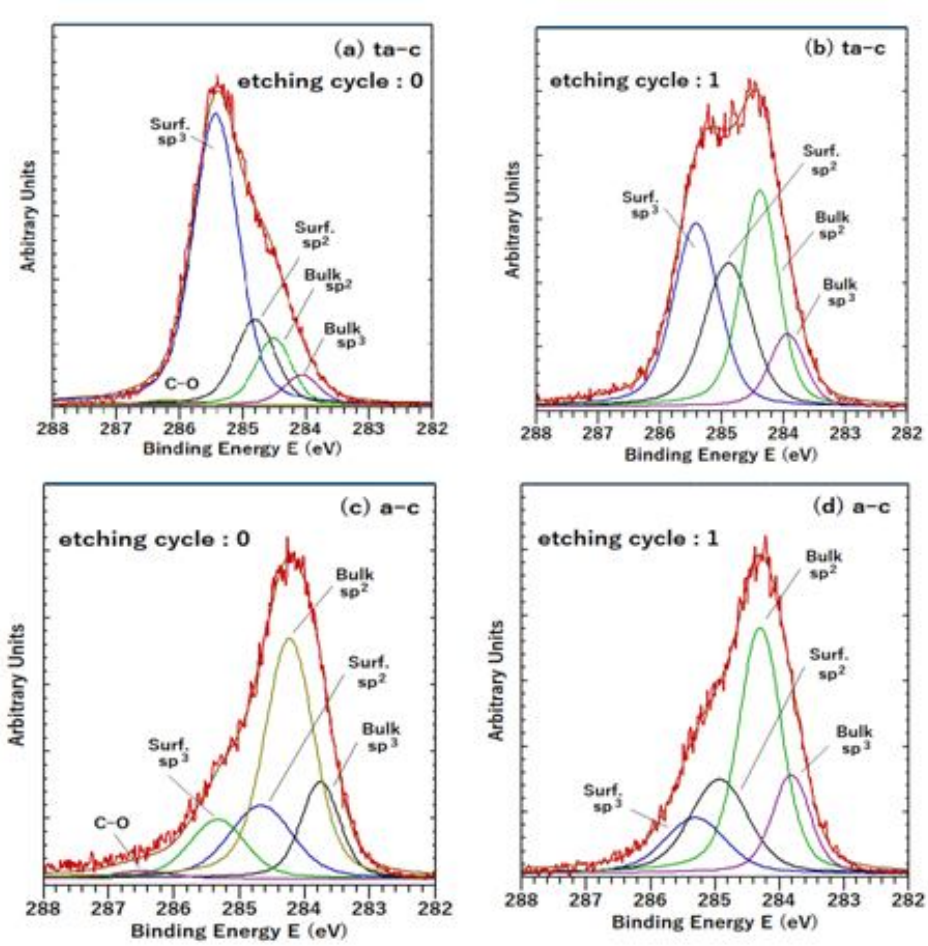

Fig. 2 Effect of etching on the components decomposed into four the XPS C1s spectra of DLC thin film.

(a) The spectra obtained from the ta-C without etching.
(b) The spectra obtained from the ta-C with etching once.
(c) The spectra obtained from the a-C without etching.
(d) The spectra obtained from the a-C with etching once.

is the main component.As shown in spectrum (b), this sp^3 surface component decreased by etching once and the sp^2 bulk component increased.On the other hand, in the case of the a-C surface, a noticeable change did not occur in the intensity distribution of the separated waveform even after the etching once.

TABLE II. List of the XPS C1s data of the DLC films (ta-C and a-C) obtained by etching cycle. (1) Binding Energy Position [eV] and Difference Δ from standard value [eV], (2) FWHM: full width-half maximum [eV], (3) %At Conc : atomic percent of the deconvolution elements.

(1)E_B position eV		no etching	etching 1	etching 2	etching 3	etching 4
ta-c	S sp^3	285.42	285.41	285.40	285.36	285.37
	S sp^2	284.80	284.89	284.84	284.77	284.78
	B sp^2	284.51	284.38	284.34	284.31	284.30
	B sp^3	284.07	283.94	283.95	283.82	283.83
a-c	S sp^3	285.33	285.37	285.35	285.33	
	S sp^2	284.66	284.86	284.85	284.73	
	B sp^2	284.23	284.28	284.31	284.30	
	B sp^3	283.75	283.79	283.88	283.86	
ta-c	Δ S sp^3	0.02	0.01	0.00	-0.04	-0.03
	Δ S sp^2	0.00	0.09	0.04	-0.03	-0.02
	Δ Bsp^2	0.21	0.08	0.04	0.01	0.00
	Δ Bsp^3	0.17	0.04	0.05	-0.08	-0.07
a-c	Δ S sp^3	-0.07	-0.03	-0.05	-0.07	
	Δ S sp^2	-0.14	0.06	0.05	-0.07	
	Δ Bsp^2	-0.07	-0.02	0.01	0.00	
	Δ Bsp^3	-0.15	-0.11	-0.02	-0.04	
(2) FWHM eV		no etching	etching 1	etching 2	etching 3	etching 4
ta-c	S sp^3	0.84	0.86	0.90	0.92	0.85
	S sp^2	0.74	0.90	0.90	0.96	0.90
	B sp^2	0.66	0.71	0.72	0.75	0.81
	B sp^3	0.67	0.68	0.76	0.66	0.69
a-c	S sp^3	1.01	0.98	1.04	0.93	
	S sp^2	1.14	0.94	0.97	0.95	
	B sp^2	0.88	0.77	0.81	0.81	
	B sp^3	0.70	0.68	0.77	0.73	
(3) %At Conc		no etching	etching 1	etching 2	etching 3	etching 4
ta-c	S sp^3	65.01	32.22	26.90	25.85	22.94
	S sp^2	16.85	26.36	26.43	24.68	21.66
	B sp^2	11.82	31.28	32.68	38.58	45.83
	B sp^3	5.29	10.14	13.99	10.89	9.57
	C-O	1.03				
	Total	100.00	100.00	100.00	100.00	100.00
a-c	S sp^3	13.88	14.75	19.55	19.37	
	S sp^2	19.38	23.75	20.81	21.67	
	B sp^2	49.4	45.38	42.55	44.69	
	B sp^3	15.66	16.12	17.09	14.27	
	C-O	1.68				
	Total	100.00	100.00	100.00	100.00	

The separated waveform data by four waveforms by etching are summarized in Table II.In order to confirm the deviation of each binding energy position, the difference from the value with sp^3surface component set to 285.4 eV, sp^2 surface component set to 284.8 eV, sp^2 bulk component set to 284.3 eV, and sp^3bulk component set to 283.9 eV from the reference value [7,8] are shown in the table II as Δ.

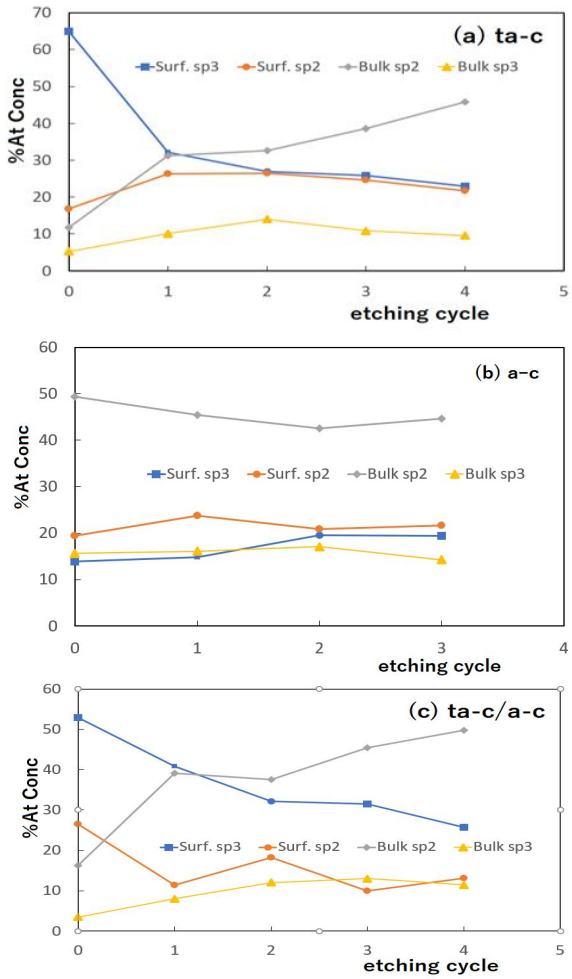

Fig.3Variation of the atomic percent of the deconvolution elements accompanying an etching cycle. (a) ta-C. (b) a-C. (c) ta-C/a-C.

Even in the spectrum without etching, the deviation of the peak position was about 0.1 eV. The FWHM were also about 0.7 to 0.9 eV.Regarding the change in atomic percent concentrationof the separate components., the change is shown in the line graph of Fig. 3.The graph (a) in Fig. 3 shows atomic percent concentration change in ta-C, indicating that the sp^3surface component decreases by etching cycle and the sp^2bulk component increases. At the a–C surface, there is almost no change in proportionof each component by the etching cycle as shown in graph (b). As a comparative experiment, a graph (c) shows the results of a sample ta-C/a-C on which ta-C was deposited on a-C.The sp^3 surface component continues to decrease by etching cycle and the sp^2 bulk component of is increased.

CONCLUSION

The C 1s XPS spectra of the DLC thin films (ta-C and a-C)while repeating the etching cycle were decomposed by waveform processing software. In case of ta-C, it was found that the sp^3 component decreases by etching and the sp^2 component increases. By making the waveform separation into four components, the sp^3surface component decreases and the sp^2 bulk component increases.It is necessary to measure detailed angle decomposition XPS and to analyze DLC sample containing hydrogen.

ACKNOWLEDGMENTS

This work was supported by TUT grant for collaborative research with Colleges of Technology and JSPS KAKENHI Grant Number 17K00997.

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