

Near-Edge X-ray Absorption Fine-Structure Characterization of Diamond-like Carbon Thin Films Formed by Various Methods

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Local structures of diamond-like carbon (DLC) films formed by various methods were studied by near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy. The DLC films are characterized by the sp^2/sp^3 ratio, which influences the mechanical and electronic properties. NEXAFS spectroscopy is sensitive to the sp^2/sp^3 ratio, because the isolated peak corresponding to the $1s \rightarrow \pi^*$ resonance transition can be observed. Carbon K-edge NEXAFS spectra for DLC thin films, which were synthesized by various methods, were measured using the total electron yield mode in the range of 275 eV–320 eV. A peak due to the coupling of carbon with oxygen was observed in the spectra of some DLC films, whereas it was not observed in the spectra of hydrogenated carbon films formed by RF sputtering. The obtained relative sp^2 contents of the DLC films were distributed in the range of $\approx 20\%$. The minimum sp^2/sp^3 ratio was obtained from DLC films formed by vacuum arc deposition from graphite, and large sp^2/sp^3 ratios were obtained from DLC films formed by plasma chemical vapor deposition from hydrocarbons. The local structure of a DLC film was concluded to depend on the synthesis method, and in particular, the carbon source material.

1. Introduction

Diamond-like carbon (DLC) films are important materials for industrial application owing to their excellent properties: high hardness, low friction, chemical inertness and good electrical insulation. The mechanical and electronic properties of DLC films are strongly

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related to the coordination of carbon atoms in films. DLC films with a high content of sp^3 -hybridized carbon, that is, a low content of sp^2 -hybridized carbon, have been used because of their high hardness. In other words, a DLC film can be characterized by the sp^2/sp^3 ratio, which is the ratio of the amount of sp^2 -hybridized carbon, $[sp^2]$, to that of sp^3 -hybridized carbon, $[sp^3]$, in the film. Therefore, the sp^2/sp^3 ratio is the most important information for understanding the properties of DLC films. Therefore, the sp^2/sp^3 ratios of DLC films were estimated by various analytical techniques such as Raman spectroscopy, X-ray photoelectron spectroscopy, Auger electron spectroscopy and electron energy-loss spectroscopy. Recently, near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy using synchrotron radiation has been utilized as an efficient method of determining the sp^2 content, $[sp^2]/([sp^2]+[sp^3])$, of DLC films.⁽¹⁻⁵⁾ The sp^2 content can be extracted from the NEXAFS spectrum with a high sensitiveness and a high quantitiveness, because the isolated peak corresponding to the carbon $1s \rightarrow \pi^*$ resonance transition can be observed.

In this work, nine kinds of DLC films were provided from the DLC research group superintended by Prof. Saitoh of Nagaoka Univ. Tech. These DLC films were formed by various methods such as vacuum arc deposition, several kinds of plasma-enhanced chemical vapor deposition and some unique methods. Carbon K-edge NEXAFS spectra of these DLC films were measured using synchrotron radiation in the soft X-ray region, and the local structures of these films were investigated.

2. NEXAFS Measurement

NEXAFS measurements were carried out at Beamline 9 (BL-9) of NewSUBARU. The electron energy of the NewSUBARU ring was 1.5 GeV during this experiment. Details of the apparatus of BL-9 were described in a previous paper.⁽⁶⁾ Briefly, undulator light provided by an 11 m undulator was extracted using a varied-line-spacing plane grating of 1200 lines/mm and was perpendicularly irradiated on the sample film. The energy resolution is estimated to be less than 0.5 eV full width at half maximum (FWHM). The monochromator output energy was calibrated using the pre-edge position, which corresponds to the carbon $1s \rightarrow \pi^*$ resonance transition, observed at 285.38 eV in the NEXAFS spectrum of graphite.⁽⁷⁾ The photocurrent from a sample was detected in the total electron yield. The intensity of incident X-rays was detected using the photocurrent from a gold mesh. The absorption signal was given by the ratio of the photocurrent from the sample to that from the gold mesh. The NEXAFS spectrum of carbon K-edge absorption was measured in the range of 275–320 eV.

3. Results and Discussion

The NEXAFS spectra of various carbon materials have been investigated previously.⁽¹⁻⁵⁾ For reference, the spectra of graphite (Toyo Tanso, IG-11) and of a commercial DLC film formed by an ion-plating method (NANOTEC) are depicted in Figs. 1 and 2, respectively. The shape of the graphite spectrum is similar to that of the graphite spectrum reported in the literature.⁽⁷⁾ In Fig. 1, a pre-edge resonance at 285.4 eV is due to transitions from the C $1s$ orbital to the unoccupied π^* orbitals principally originating from sp^2 (C=C) sites, including

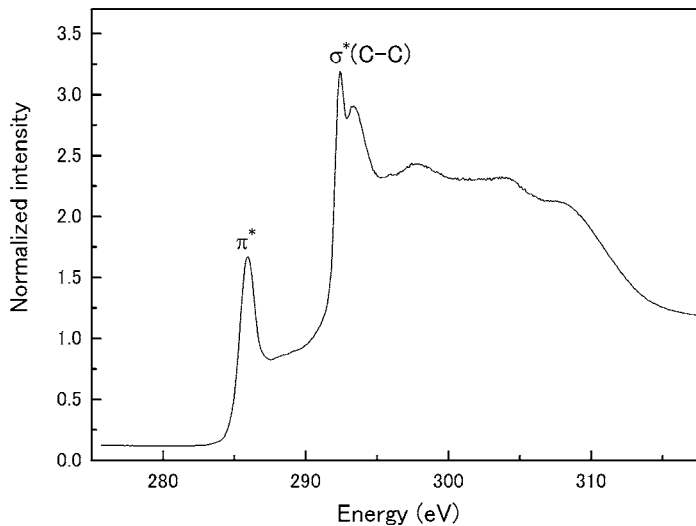


Fig. 1. C K-edge NEXAFS spectrum of graphite.

the contribution of sp ($C\equiv C$) sites if they are present. This peak is not visible in the spectrum of diamond, because diamond consists of only carbon atoms in sp^3 ($C-C$) sites. The sharp peaks located at 291.9 eV and 292.9 eV are assigned to $1s\rightarrow\sigma^*$ transitions. In the DLC spectrum, the amorphous nature of the films induces a spread of the σ^* resonance, and no recognizable structures can be identified, as shown in Fig. 2. The broad band observed in the 288–310 eV range is assignable to the result of overlapping C $1s\rightarrow\sigma^*$ transitions at the sp , sp^2 and sp^3 sites of the DLC film.⁽⁸⁾ The samples measured in the present study are summarized in Table 1 with each synthesis method, carbon source, providing laboratory and its affiliation. A reference for the synthesis procedure is cited if it has already been published. The measured C K-edge NEXAFS spectrum of each film is shown in Figs. 3–11.

A shift of the spectral position of the $1s\rightarrow\pi^*$ transition was not observed in any spectra in the present work. Two small peaks appeared in the pre-edge region (286–290 eV) of several spectra. The peak at 286.8 eV is related to the permitted $1s\rightarrow\pi^*$ transitions induced by the presence of oxygen.⁽³⁾ This peak is outstanding in Fig. 7, which shows the spectrum of a DLC film formed by the ECR plasma method (Sample E), and is also observed in Figs. 2–9. These results indicate that oxygen is easily bonded to the DLC surfaces. On the other hand, this peak was not observed in Figs. 10 and 11. These figures show the spectra of amorphous hydrogenated carbon films fabricated by RF sputtering, which were deposited in H_2/He plasmas by RF magnetron sputtering against the graphite disk (Samples H and I).⁽⁹⁾ As a result, the hydrogenated carbon surface was concluded not to couple with oxygen. Jaouen *et al.* assigned a shoulder peak located at 288.8 eV to the $1s\rightarrow\pi^*$ transitions due to $O=C-OH$ species.⁽¹⁰⁾ Gutiérrez *et al.* proposed an alternative assignment in which this peak is due to the band-edge position of amorphous carbon material.⁽²⁾ This shoulder peak appeared in Figs. 10 and 11, in which no peak due to the presence of O was observed at 286.8

Table 1

Preparation methods for sample DLC films and obtained relative sp^2 content.

Sample	Synthesis method	Carbon source	Lab.	Affiliation	Figure	sp^2 content	Ref
	Graphite			Toyo Tanso	1	0.05	
	Ion plating	benzene		NANOTEC	2	0.058	
A	Vacuum arc deposition	graphite	Hirata	Tokyo Inst. Tech.	3	0.033	11
B	Nanopulse plasma	acetylene	Ohtake	Nagoya Univ.	4	0.054	17
C	Pulse plasma	acetylene	Ohtake	Nagoya Univ.	5	0.056	18
D	RF plasma	acetylene	Ohtake	Nagoya Univ.	6	0.048	18
E	ECR plasma	methane	Saitoh	Nagaoka Univ. Tech.	7	0.041	
F	RF plasma	acetylene	Watanabe	Nippon Inst. Tech.	8	0.054	
G	RF plasma	toluene	Aono	Nat. Def. Acad.	9	0.056	12
H	RF sputtering	graphite	Higa	Ryukyu Univ.	10	0.037	9
I	RF sputtering	graphite	Higa	Ryukyu Univ.	11	0.04	9

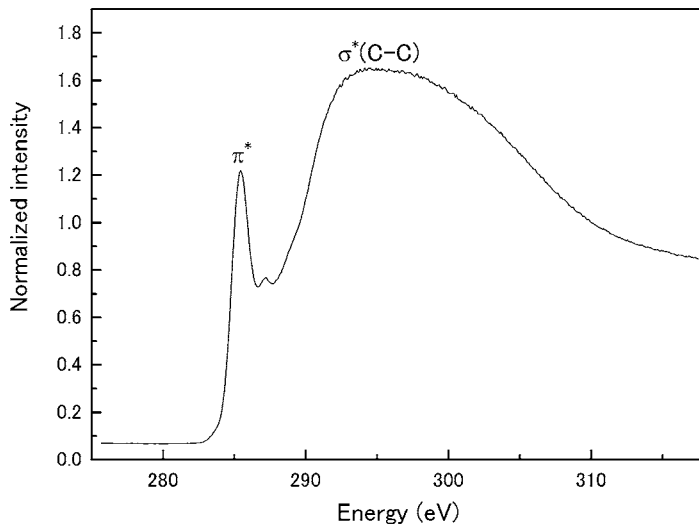


Fig. 2. C K-edge NEXAFS spectrum of commercial DLC film synthesized by ion-plating method.

eV. Therefore, the peak at 288.8 eV in these spectra was thought to be due to the latter assignment.

The spectral shape in the 288–310 eV region, which corresponds to the $1s \rightarrow \sigma^*$ resonance transition, varied for each of the observed spectra. For a typical comparison of the spectral shape of the $1s \rightarrow \sigma^*$ resonance transition between Fig. 3 and Fig. 10, the ratio of the peak intensity at 293 eV to that at 298 eV was smaller for the former than for the latter. The structure of the $1s \rightarrow \sigma^*$ resonance transition region is not fully understood. Figure 3 shows

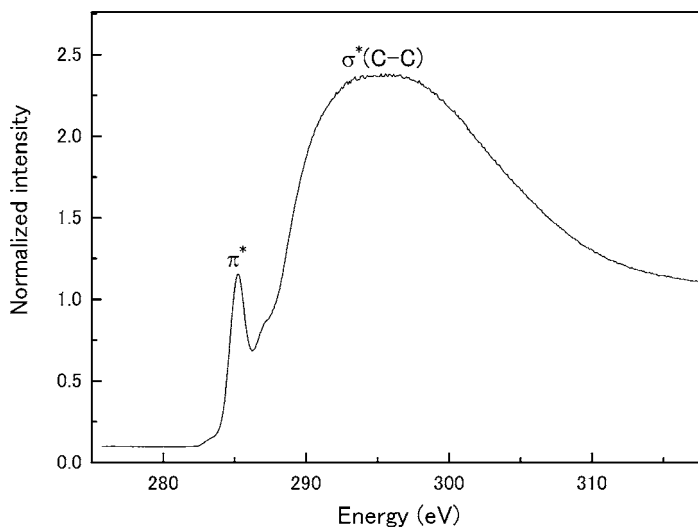


Fig. 3. C K-edge NEXAFS spectrum of sample A synthesized by vacuum arc deposition method from graphite.

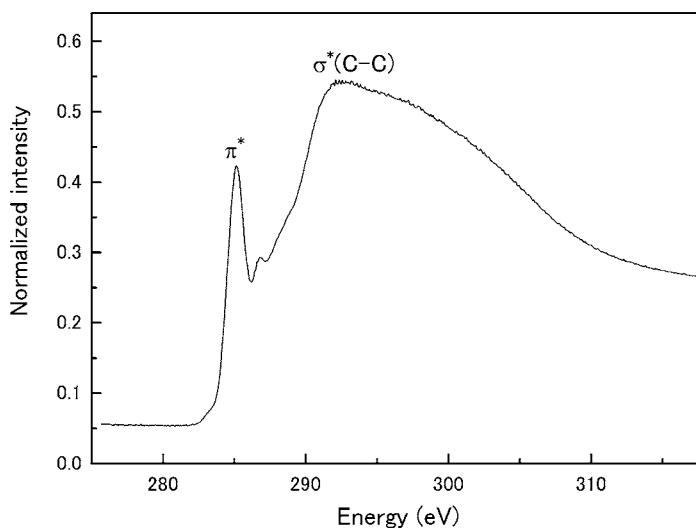


Fig. 4. C K-edge NEXAFS spectrum of sample B synthesized by nanopulse plasma method from acetylene.

the spectrum of a DLC film formed by vacuum arc deposition using graphite as a carbon source (Sample A).⁽¹¹⁾ This DLC film can be regarded as a hydrogen-free film. On the other hand, the DLC film depicted in Fig. 10 was an amorphous hydrogenated carbon film, as introduced above (Sample H). Therefore, the difference in the $1s \rightarrow \sigma^*$ region was considerable, reflecting the content of the C-H component in the film.

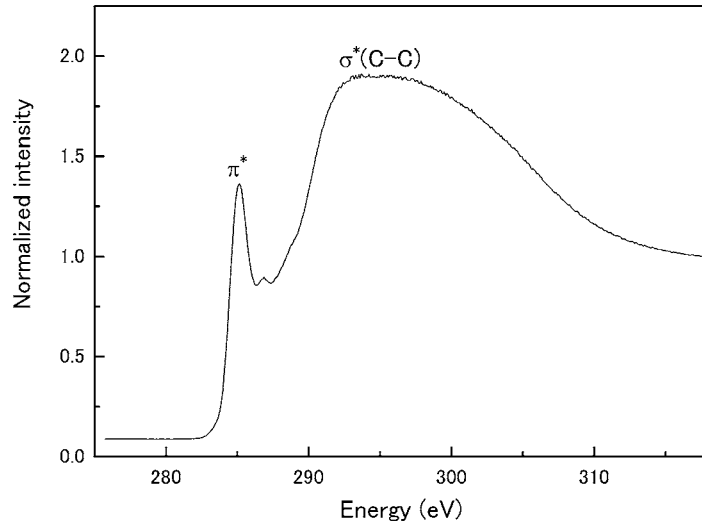


Fig. 5. C K-edge NEXAFS spectrum of sample C synthesized by pulse plasma method from acetylene.

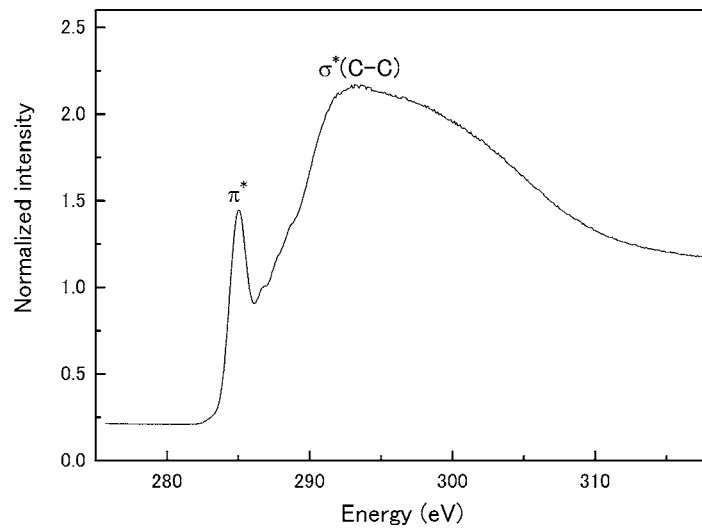


Fig. 6. C K-edge NEXAFS spectrum of sample D synthesized by RF plasma method from acetylene.

Figure 9 shows the spectrum of amorphous carbon nitride formed by RF plasma-enhanced chemical vapor deposition from nitrogen gas and toluene vapor onto a Si(100) substrate (Sample G).⁽¹²⁾ Its nitrogen content $x = \text{N/C}$ was estimated to be 0.05. NEXAFS spectra of carbon nitride film have been reported by several working groups.⁽¹³⁻¹⁶⁾ In the NEXAFS spectra of carbon nitride thin films, the peak due to transitions from the C 1s orbital

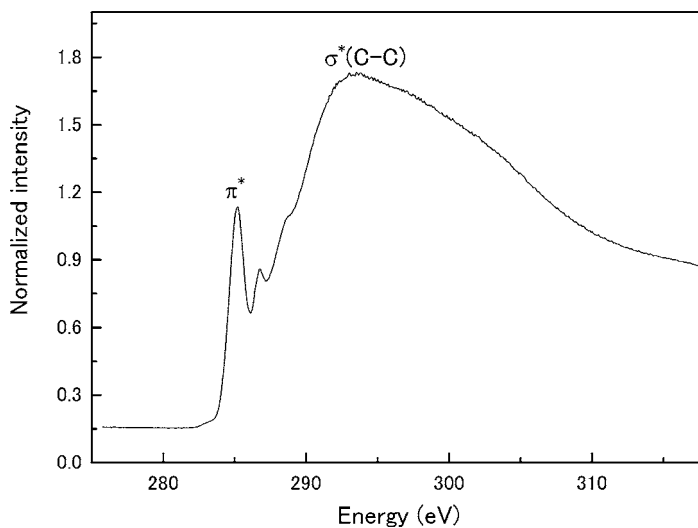


Fig. 7. C K-edge NEXAFS spectrum of sample E synthesized by ECR plasma method from methane.

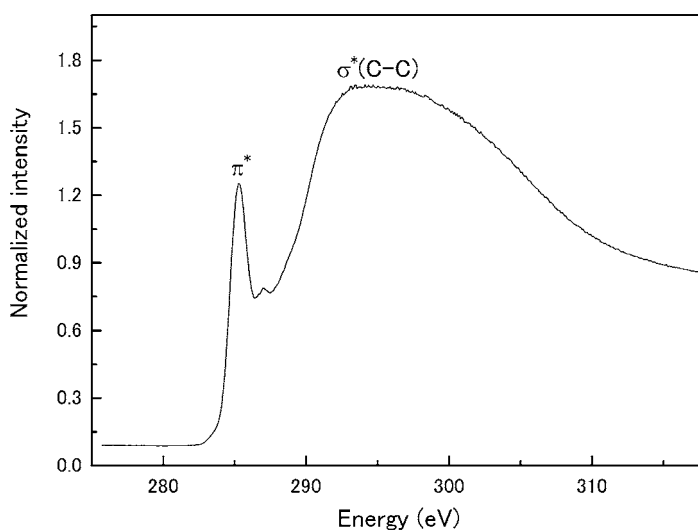


Fig. 8. C K-edge NEXAFS spectrum of sample F synthesized by RF plasma method from acetylene.

to the unoccupied π^* orbitals principally originating from C=N sites is observed at 286.6 eV. However, a small peak was observed at around 286.6 eV in Fig. 10. It is considered that the nitrogen does not affect the spectral features due to its small amount. The spectrum in Fig. 9 agrees well with the reported NEXAFS spectrum of a carbon nitride film whose nitrogen content, x , is 0.04.⁽¹⁵⁾

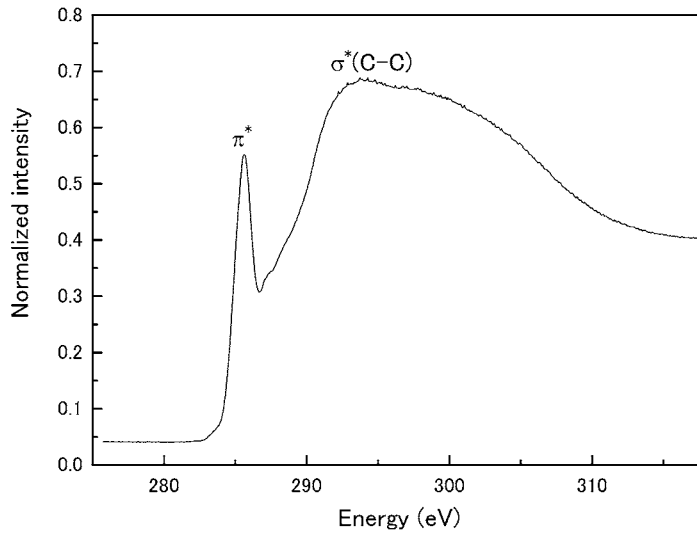


Fig. 9. C K-edge NEXAFS spectrum of sample G synthesized by RF plasma method from toluene.

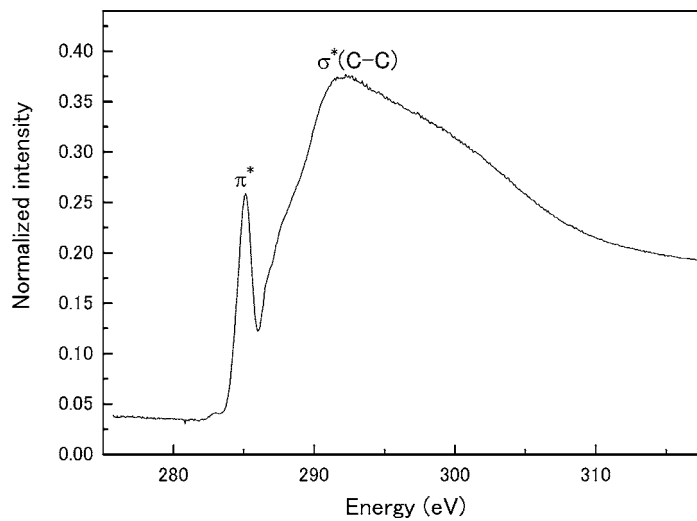


Fig. 10. C K-edge NEXAFS spectrum of sample H synthesized by RF sputtering method from graphite.

The sp^2 content obtained by the NEXAFS study is related to the hardness, which is measured using a nanoindenter.⁽⁴⁾ Namely, hardness increases monotonically with decreasing sp^2 content. Thus, the sp^2 content is a good index for DLC properties, and NEXAFS spectroscopy is a useful measurement method for the evaluation of DLC films. The method

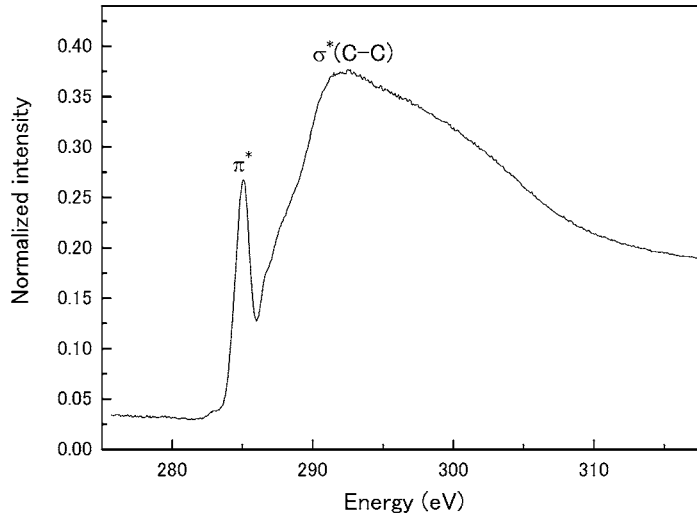


Fig. 11. C K-edge NEXAFS spectrum of sample H synthesized by RF sputtering method from graphite.

for the determination of sp^2 content from a NEXAFS spectrum was described in ref. 4. The absolute value of sp^2 content is difficult to determine, because the NEXAFS spectrum of a DLC film is very different from those of diamond and graphite, which should be used as reference materials. Thus, we evaluated DLC films on the basis of relative sp^2 content. The number of sp^2 -hybridized carbon atoms can be extracted by normalizing the area of the resonance corresponding to $1s \rightarrow \pi^*$ transitions at 285.38 eV with the area of a large section of the spectrum. The relative sp^2 content can be determined by comparing this ratio with that from another sample obtained in the same manner. The error range of the determined sp^2 content was estimated to be less than 10%. The relative sp^2 contents determined by the present measurement are tabulated in Table 1.

The minimum relative sp^2 content, that is, the maximum content of sp^3 -hybridized carbon, was obtained from the DLC film formed by the vacuum arc deposition method (Sample A). Namely, this method can provide DLC films with a high content of sp^3 -hybridized carbon. The second smallest relative sp^2 content was obtained from the amorphous hydrogenated carbon films by RF sputtering (Samples H and I). Comparatively large relative sp^2 contents were obtained from the DLC films formed by various methods of plasma-enhanced chemical vapor deposition from a hydrocarbon as a carbon source. The obtained relative sp^2 contents in the present work can be compared with those of other DLC films in ref. 4 by reference to that of the DLC film formed by the ion-plating method. We should consider the hydrogen content in the discussion of the mechanical and electronic properties of DLC films and sp^2 contents. For example, the amorphous hydrogenated carbon films in Figs. 10 and 11 can be considered to be soft and insulated from their synthesis method; however, their sp^2 contents are low, as described above. This implies that sp^3 -hybridized carbon is generated by C-H coupling in these films.

4. Conclusions

C K-edge NEXAFS spectra of DLC films formed by various methods were measured in the 275–320 eV region to compare the local structures of the films. The sp^2/sp^3 ratio was concluded to depend on the synthesis method. A DLC film formed by vacuum arc deposition from graphite was found to have a high content of sp^3 -hybridized carbon. On the other hand, DLC films formed by various plasma-enhanced chemical deposition methods from hydrocarbon molecules had a comparatively high content of sp^2 -hybridized carbon. The hydrogenated carbon surface formed by RF sputtering was found not to couple with oxygen.

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