Soft X-Ray Absorption Spectral Analysis of Amorphous Carbon and Carbon Black Using the DV-Xα Method

Yasuji Muramatsu

Abstract

The discrete variational (DV)-Xα method was used to analyze the high-resolution soft X-ray absorption spectra (XAS) in the C K-region of sputtered amorphous carbon films and carbon black to elucidate their local structures. The measured XAS of amorphous carbon and carbon black were compared with those of reference compounds, and the fine structure in the XAS can be assigned by the calculated density of states of the reference compounds. Such a comparative analysis in the measured XAS and the calculated density of states of these carbon materials with reference compounds, which have been known their local or molecular structures, is a valid approach for elucidating the complex local structures of carbon materials.

1. INTRODUCTION

Carbon materials can be usually characterized by diffraction methods (XRD, ED), microscopic methods (TEM, SEM, STM, AFM), and spectroscopic methods...
(IR, Raman, NMR, ESR, UPS, XPS, AES, EELS, SIMS) [1]. However, some industrial carbon materials such as amorphous carbon films and carbon black cannot be easily characterized from the local-structure point of view by these methods, because these materials usually take amorphous and complex structures. Recently, soft X-ray emission and absorption spectroscopy using highly brilliant synchrotron radiation [2] has been utilized to characterize various carbon materials, because information on both the occupied and unoccupied orbitals, which directly reflect the local structure and chemical states, can be provided from the high-resolution soft X-ray measurements. We have applied the soft X-ray spectroscopy to elucidate the local structure and chemical states of various carbon materials [3]. Additionally, we have successfully used the discrete variational (DV)-Xα method [4] for the soft X-ray spectroscopic analysis of the carbon materials, because the DV-Xα method can easily treat complex carbon cluster models, which should be considered for the structural analysis of amorphous carbon materials.

We have recently found that some fine structures can be commonly observed in the C K edge X-ray absorption spectra (XAS) of various sputtered amorphous carbon (a-C) films [5,6] and carbon black (CB) [7]. To clarify the spectroscopic fine structures from the local-structure and chemical-state point of view, we have compared the XAS of a-C and CB with those of reference compounds, and estimated the local structures of a-C and CB from the spectroscopic analysis using the DV-Xα method. The present paper describes one of the approaches in determining the local structure of carbon materials using the soft X-ray spectroscopy as well as the DV-Xα method.

2. SPECTROSCOPIC MEASUREMENTS AND THE DV-Xα CALCULATION

Samples of a-C films were deposited on silicon wafer substrates by various sputtering methods such as RF-sputtering, ion-beam sputtering, and electron-cyclotron-resonance (ECR) sputtering. Powder samples of CB (high abrasion furnace (HAF), semi-reinforcing furnace (SRF), super abrasion furnace (SAF), fine thermal (FT)) and reference compounds (highly oriented pyrolytic graphite (HOPG), C_{60}, C_{70}, C_{60}H_{36}, anthracene) were commercially available. XAS in the C K-region of the samples were measured in the beamline BL-6.3.2 [8] at the advanced light source (ALS). XAS were obtained by measuring the sample photocurrent, which was a total electron yield (TEY) method. The estimated resolving power (E/ΔE) of the TEY-XAS measurements was about 1600 using a 600 lines/mm variable-line-spacing grating and a 20-μm exit slit. The incident angle to the sample surface was fixed at 45° to average the orientation effect [9,10] on the spectral features resulted from oriented graphitic-structures. Energy calibration was achieved by tuning the π* peak energy of HOPG to 285.5 eV [9].

The spectral analyses were performed using the DV-Xα software. The calculated unoccupied density of states (DOS) of adequate cluster models was
compared to the measured XAS. Molecular mechanics (MM2) [11] was used to optimize the cluster model structures.

3. RESULTS AND DISCUSSION

3.1 Sputtered amorphous carbon films

Figure 16.1 shows the XAS in the C K-region of various a-C films, deposited by RF-sputtering (denoted R1–4), ion-beam sputtering (I1–3), and ECR sputtering (E1–5) methods with various sputtering conditions, and reference compounds (HOPG, C_{70}, C_{60}, and T symmetry C_{60}H_{36}). The a-C exhibited two broad peaks around 285.5 and 293 eV, which corresponded to the \( \pi^* \) and \( \sigma^* \) peaks in HOPG, respectively. Additionally four fine structures were observed between the \( \pi^* \) and \( \sigma^* \) peaks; around 284.5 eV (denoted by a), 287 eV (b), 288 eV (c), and 289 eV (d). Although the relative peak intensities among these six structures (\( \pi^* \), \( \sigma^* \), a–d) depended on the deposition methods and conditions, they were observed at constant energy positions. This suggested that certain local structures existed in the a-C films, but that their ratios varied among the films.

Some of the fine structures in the XAS of a-C corresponded to some of the fine structures of C_{70}, C_{60}, and C_{60}H_{36}. Therefore, comparing the spectral fine structures of a-C to the reference compounds, whose molecular structures are known, appears to be a valid approach for assigning these unknown fine structures and for estimating the local structure of a-C. C_{60}H_{36} is a useful compound for comparing the spectral fine structures of the a-C, because some of the fine structures (\( \pi^* \), c, d, and \( \sigma^* \)) in a-C are also observable in C_{60}H_{36}. Additionally C_{60}H_{36} can be regarded as a fairly large cluster composed of sp\(^2\)- and sp\(^3\)-C atoms. To analyze the fine structures in XAS of C_{60}H_{36}, the unoccupied DOS of the T-C_{60}H_{36} cluster model was obtained by the DV-Xa method. The left panel in Figure 16.2 shows a cluster model of T-C_{60}H_{36} and its local structure. T-C_{60}H_{36} consists of 36 sp\(^3\)-C atoms, which are bonded to H atoms, while the remaining 24 sp\(^2\)-C atoms form 4 six-membered benzene rings, which are located at the tetrahedral positions of the cage. T-C_{60}H_{36} has four types of carbon atoms. The 24 sp\(^2\)-C atoms (denoted by I) are identical, and each one is bonded to 2 sp\(^2\)-C atoms and 1 sp\(^3\)-C atom. There are three types of sp\(^3\)-C atoms: 24 of the sp\(^3\)-C atoms (II, III), each binds to 2 sp\(^3\)-C atoms, 1 sp\(^2\)-C atom, and 1 H atom, while the other 12 sp\(^3\)-C atoms (IV), each binds to 3 sp\(^3\)-C atoms and 1 H atom. The right panel of Figure 16.2 shows the unoccupied C 2p and 2s DOS of the individual sp\(^2\)- and sp\(^3\)-C atoms. The total C 2p DOS approximately reproduces the measured fine structures of the \( \pi^* \), c, d, and \( \sigma^* \) peaks in the XAS. Consequently, the fine structures can be explained by the hybridization of the 2s and 2p orbitals in the sp\(^2\)- and sp\(^3\)-C atoms. Additionally, population analysis [12] indicates that the \( \pi^* \) peak originates from the \( \pi^* \) orbitals because the 2p orbitals of sp\(^2\)-C (I) account for approximately 90% of the population at peak \( \pi^* \). For peaks c, d, and \( \sigma^* \), their orbital populations are shared by the sp\(^2\)-C (I), sp\(^3\)-C...
(II, III), and sp$^3$-C (IV) with 11–45% of 2p orbitals and up to about 11% of 2s orbitals. In particular, the 2p orbitals of both sp$^2$-C (I) and sp$^3$-C (II, III) account for more than 30% of the population at peak $c$, and the 2p orbitals of both sp$^3$-C (II, III) and sp$^3$-C (IV) account for more than 30% at peak $d$. These calculations show that peak $c$ has more sp$^2$ character than peak $d$. Peak $\sigma^*$ is mainly due to the $\sigma^*$ orbitals, which are mostly sp$^3$-C (II, III) and sp$^2$-C (I). From this analogy, it can be rationalized that the fine structures of the $\pi^*$, $c$, $d$, and $\sigma^*$ peaks in XAS of a-C are due to the hybridization of sp$^2$ and sp$^3$ carbon atoms. In addition, when a
hybridized carbon atom has the more sp\textsuperscript{3} character in the local structure, the energy position of the fine structure peak becomes higher. One plausible explanation for the lower-energy portion (fine structure, $a$) in the broad $p^\ast$ peak is discussed in the next section on carbon black, which can be estimated by nonbenzenoid structures or hydrogenated carbon atoms at the cluster edges.

### 3.2 Carbon black

Figure 16.3 shows the XAS in the C $K$-region of various CB samples and references of HOPG, C\textsubscript{60}, and anthracene. Compared to HOPG, CB shows broad spectral features, especially in the $\pi^\ast$ peak. In order to quantify the broadness of the spectral features, Figure 16.3 also shows the subtracted spectra, (CB)--(HOPG). The subtracted spectra of the CB clearly demonstrate the broad portion of the $\pi^\ast$ peak, which has peak structures at 284.2 and 286.2 eV. The energy
positions of these broad portions correspond to the $\pi^*$ features of C$_{60}$ and anthracene. It is well known that C$_{60}$ has nonbenzenoid pentagonal rings with benzenoid hexagonal rings and that anthracene has hydrogenated sp$^2$-C atoms, which form hexagonal rings at the molecular edge. From this analogy, we hypothesize that the $\pi^*$-peak broadness in CB depends on the local structures such as nonbenzenoid structures and/or hydrogenated carbon atoms at graphitic cluster edges.

Figure 16.3  Soft XAS in the C K-region of various carbon black (CB) samples (HAF, SRF, SAF, FT) and reference compounds of HOPG, C$_{60}$, and anthracene. Subtracted spectra, (CB)–(HOPG), are also shown on the absorption spectra.
To verify this idea, we calculated the DOS of some benzenoid and nonbenzenoid cluster models using the DV-Xα method. Figure 16.4 shows the benzenoid (C_{96}H_{24}) and nonbenzenoid (C_{80}H_{20}, C_{112}H_{28}) cluster models, and their DOS in the unoccupied C 2p and C 2s orbitals from the centered carbon atoms (numbered as 1C) to the edged atoms (as 7C). In the nonbenzenoid cluster models, C_{80}H_{20} and C_{112}H_{28}, the central 1C atoms form a pentagonal ring and a heptagonal, respectively. In the C 2p-DOS, the central 1C atoms in the nonbenzenoid pentagonal and heptagonal rings exhibit a lower-energy DOS at

![Figure 16.4](image)

**Figure 16.4** Upper panel shows a benzenoid cluster model (C_{96}H_{24}) and nonbenzenoid models (C_{80}H_{20}, C_{112}H_{28}). Lower panel shows the unoccupied C 2p-DOS and C 2s-DOS of carbon atoms in the cluster models. Carbon atoms from the centered atoms to the edged atoms are numbered as 1C–7C, respectively. Hydrogen atoms terminating the edged-carbon atoms are numbered as 8H. The lower-energy DOS portions at the π* peak positions of 1C and 7C are denoted by arrows. For a colour version of this figure please see the colour plate section near the end of the book.
Figure 16.5  Upper panel shows a molecular model for anthracene \( \text{C}_{14}\text{H}_{10} \). Four types of C atoms are numbered as 1C–4C. Lower panels show the unoccupied C 2p-DOS and C 2s-DOS of the numbered carbon atoms and all carbon atoms.
the $\pi^*$ positions compared to the hexagonal ring in the benzenoid cluster model. In addition, hydrogenated 7C atoms in both the benzenoid and nonbenzenoid cluster models exhibit similar lower-energy DOS at the $\pi^*$ position compared to the center 1C atoms in the benzenoid cluster model. These lower-energy DOS portions, which are due to the nonbenzenoid structures and hydrogenated carbon atoms, correspond to the measured broad $\pi^*$ peak features of CB; especially the 284.2 eV peak observed in the subtracted spectra of (CB)–(HOPG).

Figure 16.5 shows the molecular structure of anthracene and its DOS. In this model, the carbon atoms numbered as 1C, 2C, and 3C are hydrogenated atoms and the 4C atoms does not bond to hydrogen. Although the hydrogenated 1-3C atoms exhibit lower-energy DOS at the $\pi^*$ positions, the 4C atoms does not exhibit the lower-energy DOS. These edged carbon atoms also exhibit a higher-energy DOS at the $\pi^*$ position. This shows that the carbon atoms at cluster edges can result in the $\pi^*$-peak broadness, and especially the hydrogenated atoms can result in the lower-energy broadening at the $\pi^*$ peak. These broad DOS features correspond to the measured broad portions of the $\pi^*$ peak in the XAS of CB.

Consequently, it has been confirmed that the broad $\pi^*$ peak features in the XAS of CB can provide local structure information, especially on the nonbenzenoid structure and/or hydrogenated cluster-edged carbon atoms.

4. CONCLUSION

To elucidate the local structures of sputtered a-C films and CB, we measured their high-resolution soft XAS in the C K-region and analyzed the spectral fine structures by the DV-Xα method. Sputtered a-C films exhibit fine structures between the $\pi^*$ and $\sigma^*$ peaks in the measured XAS. Some of the fine structures in the a-C correspond to those of C$_{60}$H$_{36}$. From the analogy between the a-C and C$_{60}$H$_{36}$, it can be considered that the fine structures in XAS of a-C results from the hybridization of the sp$^2$- and sp$^3$-C atoms and that the higher-energy structures between $\pi^*$ and $\sigma^*$ peaks has more sp$^3$ character and less sp$^2$ character than the lower-energy structures. CB exhibits the broad $\pi^*$ features that correspond to some of the fine structures at the $\pi^*$ peaks of C$_{60}$ and anthracene. From the calculated DOS of the nonbenzenoid cluster models and anthracene, the broad $\pi^*$ peak feature of CB can be explained by the nonbenzenoid structures and/or hydrogenated carbon atoms at the cluster edges.

Although the complex local structure of carbon materials cannot be easily or completely elucidated by conventional analysis methods, the high-resolution soft X-ray absorption spectroscopy and spectral analysis using the DV-Xα method are promising tools to analyze the local structure. In addition, comparative analysis of carbon materials with reference compounds that have been known their local and molecular structures is a valid approach for elucidating the local structure.
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REFERENCES