Soft X-ray Absorption Spectra of Amorphous Carbon

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Abstract

Information about the local-structure of amorphous carbon (a-C) films was obtained by comparing soft X-ray absorption spectra in the CK region of sputtered a-C films to reference carbon compounds such as hydrofullerene (C60H36), highly oriented pyrolytic graphite (HOPG), and carbon black. The spectra of the a-C films contained two main structures, which consisted of at least different six portions. Comparing the spectral features of the a-C films with the reference compounds and the spectral analysis by discrete variational (DV)-Xs molecular orbital calculations indicated that the fine structures of the a-C films are due to a hybrid of sp2 and sp3 carbon atoms.

1. Introduction

Amorphous carbon (a-C) films are important and interesting materials in industry and materials science. It is believed that they consist of a random structure of sp2 and sp3-configured carbon atoms and that the local structure or chemical bonding states determine their mechanical and optical properties. Thus, numerous researchers have conducted characterization studies of a-C films using various analytical methods such as Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS) in order to clarify local structures and chemical bonding states. Recently, various carbon films have been characterized by soft X-ray emission and absorption spectroscopy using highly brilliant synchrotron radiation [1–6]. This method is effective for obtaining electronic-structure information about occupied and unoccupied orbitals, which directly reflects the local structure and chemical bonding states. However, the spectral features observed in the X-ray emission and absorption spectra of the a-C films have yet to be clearly assigned.

In our previous study [6], fine structures were clearly observed in the soft X-ray absorption spectra of sputtered a-C films, which were systematically deposited by various sputtering methods under varying conditions. These fine structures have rarely been measured by EELS [7, 8], which generally has a lower energy resolution than soft X-ray absorption spectroscopy using synchrotron radiation. Thus, in order to extract information on the local structures of a-C films from the fine structures, soft X-ray absorption spectroscopy of a-C films were compared to reference carbon compounds. Reference compounds should be selected if they are fairly large molecules, which were composed of sp2 and sp3 carbon atoms. Hence, this study used hydrofullerene (C60H36), which is composed of twenty-four sp2 carbon atoms and thirty-six sp3 carbon atoms, as the reference compound.

This paper describes the comparison on the soft X-ray absorption spectral features between a-C films and reference compounds such as C60H36, highly oriented pyrolytic graphite (HOPG), and carbon black.

2. Experiments

The total-electron-yield (TEY) X-ray absorption spectra in the CK region of commercially available T-symmetry C80H60 [9], HOPG, and carbon black were measured in beamline BL-6.3.2 [10] at the Advanced Light Source (ALS). Powder samples of C60H36 and carbon were pressed and held on indium-sheet substrates. The estimated resolving power (E/ΔE) of the TEY absorption measurements was approximately 1600 using a 600lines/mm variable-line-spacing grating and a 20μm exit slit. The incident angle to the sample surface was fixed at 45 degrees. The measurement conditions were the same as the previous measurement of sputtered a-C films [6]. The energy calibration was achieved by tuning the 4p peak energy of HOPG to 285.5 eV.

3. Results and Discussion

Figure 1 shows the TEY X-ray absorption spectra of the a-C films and reference compounds, C60H36, HOPG, and carbon black. The spectra of the a-C films were extracted from previously measured data [6]. The a-C films were deposited by RF, ion-beam, and electron-cyclotron-resonance (ECR) sputtering methods under various deposition conditions. For the RF-sputtered carbon films, the pressure of the source gas was 5×10−3 Torr (R1), 1×10−2 Torr (R2), and 1×10−2 Torr (R3). For the ECR-sputtered carbon films, the annealing temperature was ‘not annealed’ (I1), 400°C (I2), and 700°C (I3). For the ECR-sputtered carbon films, the acceleration voltage was −20 kV (E1), −75 kV (E2), and −100 kV (E3). The spectra of a-C films displayed two peaks at 285.5 eV and 293 eV, which correspond to the energy portions of π* and σ* peaks in HOPG, respectively. Therefore, these peaks in a-C films are assigned to be π* and σ* peaks, respectively. Four other structures are also observed at 284.5 eV (denoted by a), at 287 eV (b), at 288.5 eV (c), and at 289 eV (d) among the a-C films. Although the relative peak intensities among these six structures depended on the deposition methods/conditions, the peaks were observed at constant energy positions, which suggests common local structures in the a-C films, but at different ratios. Similar structures, which correspond to the π*, c, d, and σ* in C60H36, were noted in the spectral feature of the a-C films. Therefore, it is estimated that the a-C films have local structures similar to C60H36. A broad π* peak is observed in carbon black at 285.5 eV and the energy position of the lower-energy portion in this π* peak corresponds to the lowest-energy fine structure in a-C films. Carbon black is essentially formed from randomly-ordered polycyclic-aromatic-structures [11]. Hence, it is estimated that similar polycyclic-aromatic structures partially exist in a-C films.

The local structures of a-C films were further estimated by comparing the spectral similarities to the spectral features of C60H36, which were analyzed by discrete variational (DV)-Xs molecular orbital calculations [12–13]. Figure 2 shows...
the molecular structure of the $T$-symmetry $C_60H_{36}$ and its local structure. In $T$-$C_60H_{36}$, thirty-six of the carbon atoms are bound to hydrogen atoms that have a sp$^3$ configuration. The remaining twenty-four carbon atoms are sp$^2$ and form four six-membered benzene rings located in the tetrahedral positions. There are four structurally unique carbon atoms in $T$-$C_60H_{36}$. The twenty-four sp$^2$-C atoms (I) are identical and each is bound to two sp$^2$-C atoms, one sp$^2$-C atom, and one H atom. The other twelve sp$^3$-C atoms (IV) are each bound to three sp$^3$-C atoms and one H atom. For the spectral analysis of the X-ray absorption, DV-Xα MO calculations on the electronic structure of the excited states, with the inner core holes and electrons in unoccupied orbitals, should be necessary to exactly reproduce the measured X-ray absorption spectral features [14]. However, the calculations on excited states are generally more difficult than those on the ground states, and the ground-state calculations provide approximated information on the X-ray spectral analysis especially in K-shell excitations. Thus, we show here the calculated spectra on the ground states as the first-order approximation. Figure 3 shows the unoccupied C2p- and C2s-DOS spectra of the individual sp$^2$- and sp$^3$-C atoms. The total C2p-DOS spectrum approximately reproduces the measured X-ray spectral features of $\sigma^*$, $c$, $d$, and $\sigma^*$. Table I lists the unoccupied orbital populations of the individual carbon atoms. The $\pi^*$ peak originates from $\sigma^*$ orbitals since the 2p orbitals of the sp$^2$-C (I) account for approximately 90% of the population at peak $\pi^*$. The orbital populations of peaks $c$, $d$, and $\sigma^*$ peaks are shared by sp$^2$-C (I), sp$^3$-C (II, III), and sp$^3$-C (IV) with 11–45% of the 2p orbitals and up to 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 peak $d$. This indicates that peak $c$ has more sp$^2$ character than peak $d$. The $\sigma^*$ peak is mainly due to the $\sigma^*$ orbitals, which are mostly composed of sp$^3$-C (II, III) and sp$^3$-C (IV) account for less than 30% of peak $d$. From this analogy, it can be estimated that the fine structures $\sigma^*$, $c$, $d$, and $\sigma^*$ in $a$-C films result from the hybridization of sp$^2$ and sp$^3$ carbon atoms. In addition, the higher the energy positions of the fine structure peaks, the more sp$^3$ character the hybridized carbon atoms have in the local structure.

4. Conclusion
The soft X-ray absorption spectra of $a$-C films, which were measured using synchrotron radiation, were compared to
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Fig. 3. Calculated total DOS spectrum and DOS spectra of individual carbon atoms (I–IV) in T-C60H36. The measured X-ray absorption spectra are also shown on the total DOS spectrum.

reference compounds, T-C60H36, HOPG, and carbon black. The a-C films had fine structures, which consisted of at least six portions. Four portions (α*, c, d, and σ*) in the fine structure corresponded to the energy positions of four peaks in T-C60H36. Spectral analysis of T-C60H36 using DV-Xα MO calculations indicated that the origin of these peaks is the hybridization of sp2 and sp3 carbon atoms. Therefore, it is estimated that the fine structures observed between T-C60H36 and sp3 carbon atoms. The lowest-energy fine structure α in a-C films corresponded to the lower-energy portion in the broad peak in carbon black.

Table I. Orbital populations of the four different types of carbon atoms (I–IV) in unoccupied orbitals corresponding to the measured X-ray absorption peaks denoted by α*, c, d, and σ*.

<table>
<thead>
<tr>
<th>Orbital population</th>
<th>( \text{sp}^2 \text{-C(I)} )</th>
<th>( \text{sp}^3 \text{-C(II&amp;III)} )</th>
<th>( \text{sp}^3 \text{-C(IV)} )</th>
<th>( \text{MO energy} / \text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>α*</td>
<td>5.2</td>
<td>0.6</td>
<td>90.6</td>
<td>11</td>
</tr>
<tr>
<td>c</td>
<td>10.4</td>
<td>8.6</td>
<td>3.1</td>
<td>31.9</td>
</tr>
<tr>
<td>d</td>
<td>13.2</td>
<td>10.4</td>
<td>2.3</td>
<td>11.1</td>
</tr>
<tr>
<td>σ*</td>
<td>13.2</td>
<td>13.2</td>
<td>6.1</td>
<td>17.9</td>
</tr>
</tbody>
</table>

Hence, it is estimated that the lowest-energy fine structure α in the a-C films originated from polycyclic-aromatic-structures. The reference compounds did not display the fine structure b. Thus, further experiments using different reference compounds are necessary to estimate the origin of the fine structures in a-C films.

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