Local Structure Analysis on Si-Containing DLC Films Based on the Measurement of C K-Edge and Si K-Edge X-ray Absorption Spectra

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Abstract: In this paper, the local structure of silicon-containing diamond-like carbon (Si-DLC) films is discussed based on the measurement of C K-edge and Si K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra using the synchrotron radiation of 11 types of Si-DLC film fabricated with various synthesis methods and having different elemental compositions. In the C K-edge NEXAFS spectra of the Si-DLC films, the σ* band shrunk and shifted to the lower-energy side, and the π* peak broadened with an increase in the Si content in the Si-DLC films. However, there were no significant changes observed in the Si K-edge NEXAFS spectra with an increase in the Si content. These results indicate that Si–Si bonding is not formed with precedence in Si-DLC film.

Keywords: Si-containing diamond-like carbon film; near-edge X-ray absorption fine structure; dependence on the elemental composition

1. Introduction

Diamond-like carbon (DLC) film is amorphous carbon (a-C) film, which has a disordered form of C consisting of sp2 and sp3 hybridized bonds [1, 2]. DLC films are widely used as coating materials in various industrial fields due to their superior properties, such as their high hardness, low friction coefficient, chemical inertness, and gas barrier [3–5]. Over the last two decades, various novel DLC films have been synthesized for several industrial purposes. Hetero-atom-containing DLC films were developed because the existence of hetero-atoms in DLC film has the potential to improve the film properties. In particular, the incorporation of Si into DLC films has resulted in an increase in thermal stability [6, 7] and resistance to oxidation [8, 9], and a decrease in friction in a humid atmosphere [10–12] and intrinsic stresses [13, 14]. Therefore, silicon-containing DLC (Si-DLC) films have attracted an increasing amount of attention in various industrial fields due to these properties [15–18].

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy using synchrotron radiation is known to be sensitive to the local structure around the absorber atom. In near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, the out-coming current from the sample is recorded as a function of the photon excitation energy around the core level of the target element using synchrotron radiation. Transitions occurring via the unoccupied states of the x-ray absorbing elements, whose energy shifts are large, can be observed in this technique. Therefore, NEXAFS is known to be sensitive to the local structure around the absorber atom, in comparison with other spectral evaluation methods. It also does not require long-range ordering and is sensitive to the local bonding structure. Therefore, NEXAFS
spectroscopy is an adequate method for evaluating DLC films, which have an amorphous structure. The NEXAFS spectra of Si-DLC films have also been measured, e.g., C K-edge NEXAFS spectra [19–23] and Si K-edge NEXAFS spectra [24,25]. We previously reported a comprehensive analysis on Si-DLC films based on the measurements of C K-edge NEXAFS spectra [26]. In the present study, we measured the C K-edge NEXAFS spectra and Si K-edge NEXAFS spectra of 11 types of Si-DLC film fabricated using various synthesis methods. The elementary analysis was conducted using a combination of Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA). We discuss the composition ratio of Si dependency on the local structure and the chemical environments of C and Si in Si-DLC films.

2. Materials and Methods

We analyzed 11 types of Si-DLC film, which were provided by enterprises, public organizations, and universities, by measuring the C K-, Si K-, and Si L-edge NEXAFS spectra. These DLC samples were collected by the DLC research group in Japan, which has been working on the classification of DLC films [27]. The Si-DLC films were deposited on Si substrates by using various methods, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). The desired film thickness was 200 nm.

The RBS and ERDA measurements were performed using an electrostatic accelerator (NT-1700HS: Nisshin-High Voltage Co., Kyoto, Japan) located at the Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Japan. Details of RBS and ERDA measurements are described in refs. [28–30]. The He⁺ ions accelerated to 2.5 MeV were used as the incident beam at 72° with respect to the normal surface of a sample. In the RBS measurement, a small fraction—0.1%—of high-energy He⁺ ions elastically scattered by the sample were captured with a solid-state detector (SSD) arranged at 12° with respect to the normal surface of a sample toward the incident beam. RBS was applied to determine the atomic fractions of C and Si in the samples. In the ERDA measurement, the He⁺ ions elastically collided with H atoms in a sample. The H atoms that were ejected from a sample were detected with an SSD placed at 78° to the normal surface of a sample in the opposite direction to the incident beam. RBS and ERDA signals were simultaneously detected and ERDA was applied to determine the atomic fraction of H in the samples. The estimation error of the RBS/ERDA measurement was 0.5 at.%, because the determination of the content was simulated in 1 at.% steps. The obtained elemental compositions of these samples are listed in Table 1. The ratios of Si/(C + Si) in these films ranged from 0.03 to 0.39.

| Sample | H Content (at.%) | Si Content (at.%) | Si/(C + Si) | sp²/(sp² + sp³) |
|--------|-----------------|------------------|------------|----------------|
| 1      | 23              | 2                | 0.03       | 0.61           |
| 2      | 22              | 5                | 0.07       | 0.64           |
| 3      | 20              | 7                | 0.09       | 0.55           |
| 4      | 19              | 7                | 0.09       | 0.31           |
| 5      | 22              | 8                | 0.11       | 0.58           |
| 6      | 29              | 12               | 0.17       | 0.50           |
| 7      | 26              | 15               | 0.20       | 0.44           |
| 8      | 27              | 15               | 0.21       | 0.50           |
| 9      | 41              | 14               | 0.23       | 0.16           |
| 10     | 20              | 18               | 0.23       | 0.63           |
| 11     | 33              | 26               | 0.39       | 0.37           |
NEXAFS measurements were carried out at the NewSUBARU synchrotron facility of the University of Hyogo [31]. The Si K-edge NEXAFS spectra were measured at beamline 05A, where synchrotron radiation provided by a bending magnet was dispersed using a double crystal monochromator (DXM) [32]. The Si K-edge NEXAFS spectra were measured in the energy range from 1830 to 1880 eV using InSb (111) as a dispersive crystal. The Si L- and C K-edge NEXAFS spectra were measured at beamline 09A, where synchrotron radiation provided by an 11-m undulator was dispersed using a varied spacing planer-grating monochromator [33–35]. The Si L-edge and C K-edge NEXAFS spectra were measured in the energy range from 90 to 120 eV and from 275 to 335 eV, respectively. At both K edges, monochromatized synchrotron radiation was irradiated on the sample at 54.7° (magic angle) with respect to the normal surface of a sample. All NEXAFS spectra were measured with the total electron yield (TEY) mode. The electrons coming from the sample were detected by measuring the current from the earth to the sample, \( I_0 \). The intensity of the incident photon beams, \( I_0 \), was measured by monitoring the photocurrent from a gold mesh, which was placed in front of the sample. The absorption signal was obtained by the ratio between the out-going electron intensity from the sample, \( I_s \), and \( I_0 \). In order to support the correctness of the measurements, all NEXAFS spectra of each sample were recorded at a minimum of three locations.

3. Results and Discussion

Figure 1 shows the measured C K-edge NEXAFS spectra of the 11 Si-DLC film samples. The spectra are displayed from the highest (top) to lowest (bottom) Si/(C + Si) ratio. Figure 2 shows the C K-edge NEXAFS spectrum of the Si-DLC film that had the highest content of Si (sample 11), along with those of diamond powder, HOPG, \( \beta \)-SiC powder, and a typical commercial DLC film that was deposited on a 200 nm-thick Si wafer by using the ion plating method. The sharp \( \pi^* \) peak observed at 285.38 eV in the C K-edge NEXAFS spectra of HOPG is ascribed to the C1s→\( \pi^* \) resonance transition originating from the C=C bonds [36]. The peak of the C1s→\( \pi^* \) resonance transition was observed at 284.4 eV in the typical DLC film. This peak was not observed in the C K-edge NEXAFS spectra of diamond powder and \( \beta \)-SiC powder. Structural peaks were observed in the 285–310 eV region of the C K-edge spectra of HOPG, diamond powder, and \( \beta \)-SiC powder. The peaks in the spectra of diamond powder and \( \beta \)-SiC powder are ascribed to the C1s→\( \sigma^* \) resonance transition generated from the C=C bonds and the C–Si bonds, respectively [36–38]. The peaks in the spectra of HOPG are ascribed to the C1s→\( \sigma^* \) resonance transition generated from the C–C bonds and C=C bonds. In the C K-edge spectra of the DLC film and Si-DLC film, the C1s→\( \sigma^* \) resonance transition generated from the C–C bonds, C=C bonds, or C–Si bonds was observed as a broad band at about 285–320 eV, because DLC and Si-DLC have amorphous structures.

The spectral profiles of the C K-edge NEXAFS spectra of the Si-DLC films were reported to change along with the ratio of Si/(C + Si) in the films [26]. As the Si/(C + Si) ratio increases in the film, 1) the \( \sigma^* \) band shrinks due to the change from \( \sigma(C-C) \) to \( \sigma(C-Si) \) and 2) broadening of the \( \pi^* \) peak can be seen due to an increase in the composition ratio of C=C–Si sites.

The \( sp^2/(sp^2 + sp^3) \) ratio of carbon atoms in DLC films is the most important information for understanding the properties of such films. This ratio depends on many factors, such as the deposition method and deposition condition. The \( sp^2/(sp^2 + sp^3) \) ratio decreases with an increasing H content in DLC film [39]. The absolute \( sp^2/(sp^2 + sp^3) \) ratio of C atoms in DLC film can be determined with a high accuracy because the 1s→\( \pi^* \) resonance transition can be separately observed in the C K-edge NEXAFS spectrum [39–41]. The amount of \( sp^2 \) hybridized C atoms can be extracted by normalizing the area of resonance corresponding to the 1s→\( \pi^* \) transitions at 285.4 eV with a large section of the spectrum. The absolute \( sp^2/(sp^2 + sp^3) \) ratio was determined by comparing it with that from the NEXAFS spectrum of HOPG, which can be regarded as the full construction of \( sp^2 \) hybridized C. The \( sp^2/(sp^2 + sp^3) \) ratios estimated from the C-K edge NEXAFS spectra of the Si-DLC films are summarized in Table 1. These values are the average \( sp^2/(sp^2 + sp^3) \) ratio obtained from C-K edge NEXAFS spectra measured at three locations of each sample. It was reported that the \( sp^2/(sp^2 + sp^3) \) ratios of the Si-DLC films gradually
decreased with an increasing Si/(C + Si) ratio in our previous study [26]. It can be considered that Si atoms only coupled to C atoms by single bonding in Si-DLC films. The present results are almost in accordance with this tendency; however, several exceptions, for example, sample 10, were obtained. The $sp^2/(sp^2 + sp^3)$ ratios of carbon films depend on the deposition method, deposition condition, density, and hydrogen content. In sample 10, the $sp^2/(sp^2 + sp^3)$ ratio was considered to be lowered by its high content of hydrogen.

Figure 1. C K-edge NEXAFS spectra of 11 types of Si-DLC film samples. Spectra are displayed from the highest (top) to lowest (bottom) Si/(C + Si) ratio.

Figure 2. C K-edge NEXAFS spectra of Si-DLC film (sample 11), diamond powder, HOPG, typical DLC film, and $\beta$-SiC powder.

Figure 3 shows the Si K-edge NEXAFS spectra of the 11 Si-DLC film samples. The spectra are displayed in the same order as in Figure 1. Figure 4 shows the Si K-edge spectra of sample 11, along with those of SiO$_2$ powder, $\beta$-SiC powder, a-Si:H film, and Si wafer. The energy of the first inflection point, $E_0$, and that of the white line, representing an electronic Si $1s \rightarrow \pi_2$ transition, $E_{\text{max}}$, depend on the electronegativity of the atoms surrounding the Si [38]. These energies shift towards a higher energy.
with an increasing positive charge on the absorber. An intense sharp peak was observed at 1846.8 eV in the spectrum of SiO2 powder [42]. The E0 and Emax of the Si-DLC film were slightly higher than those of the Si wafer and a-Si:H film, much lower than those of SiO2 powder, and similar to those of SiC, as reported by V. Palshin et al. [25]. As shown in Figure 3, E0, Emax, and other spectral features did not vary systematically along with the Si/(C + Si) ratio in the present study.

![Figure 3](image_url) Si K-edge NEXAFS spectra of 11 types of Si-DLC film samples. Spectra are displayed from the highest (top) to lowest (bottom) Si/(C + Si) ratio. A filled arrow and open arrow indicate the position of E0 and Emax of the Si 1s→t2 transition, respectively.

![Figure 4](image_url) Si K-edge NEXAFS spectra of Si-DLC film (sample 11), SiO2 powder, β-SiC powder, a-Si:H film, and Si wafer. Filled arrows and open arrows indicate the position of E0 and Emax of the Si 1s→t2 transition, respectively.
Figure 5 shows the Si L-edge NEXAFS spectra of the 11 Si-DLC film samples. Figure 6 shows the Si L-edge NEXAFS spectra of sample 11, along with those of SiO₂ powder, β-SiC powder, a-Si:H film, and Si wafer. In the spectrum of SiO₂, characteristic peaks were observed at 105.4, 106.0, and 107.8 eV, which were assigned to the transitions 2p₃/₂ → a₁, 2p₁/₂ → a₁, and 2p → t, respectively [43]. These characteristic peaks derived from oxidized Si were observed in the Si L-edge spectra of samples 3 and 10, as shown in Figure 5, and those of a-Si:H film and Si wafer in Figure 6. These samples were obviously oxidized naturally. However, the characteristic peak derived from oxidized Si, which was observed at 1846.8 eV in the Si K-edge spectrum of SiO₂ powder, was not observed in the Si K-edge NEXAFS spectra of the above samples. This discordance is ascribable to the difference in the detection depth of Si K-edge, with a value of ~1850 eV, and Si L-edge, with a value of ~100 eV. Natural oxidation of these samples was considered to occur in the neighborhood of the surfaces of each sample. The energy of the first inflection point, E₀, of L-edge elemental Si is 100 eV and that of silicon oxide is 105 eV [43]. The E₀ of L-edge of the Si-DLC films, which are not oxidized, is ≈104 eV. This resembled that of SiC, is higher than those of Si wafer and a-Si:H film, and is lower than that of SiO₂ powder. The relation of E₀ positions due to the materials is similar to that in the Si K-edge.

As described above, the chemical environment of C atoms varied along with the Si/(C + Si) ratio in the Si-DLC film. However, that of Si atoms was not affected by this ratio. These results indicate that Si atoms in the Si-DLC film dominantly bonded to C atoms in the Si/(C + Si) region, with a value of less than 0.39. In other words, Si–Si bonding did not occur in this Si/(C + Si) ratio region. Palshin et al. concluded that Si atoms in Si-DLC films are surrounded by four C atoms, as revealed by Si K-edge extended x-ray absorption fine structure (EXAFS) measurement [25]. The measurements in the present study agree with their conclusion. However, the Si/(C + Si) ratio of the Si-DLC films they used was 0.125, but that of sample 11 in the present study was ≈0.4. In Si-DLC film with an Si/(C + Si) ratio of 0.39, the DLC structure cannot be constructed without coupling of the Si–Si bond. Therefore, the Si K- and L-edge NEXAFS spectra do not depend on the Si/(C + Si) ratio in Si-DLC films. Additionally, not only do Si atoms tend to enter between C atoms, but the chemical environment of an Si atom coupled to a C atom is close to that of an Si atom coupled to Si atoms, as shown in Figure 4.

Figure 5. Si L-edge NEXAFS spectra of 11 types of Si-DLC film samples. Spectra are displayed from the highest (top) to lowest (bottom) Si/(C + Si) ratio.
4. Conclusions

In this study, we investigated the local structure of Si-DLC films by measuring the C K-edge and Si K-edge NEXAFS spectra of 11 types of Si-DLC film with Si/(C + Si) ratios ranging from 0.03 to 0.39. The spectral features of the C K-edge NEXAFS spectra of the Si-DLC films varied along with the Si/(C + Si) ratio: 1) the σ* band at 275–335 eV shrank and 2) the π peak at 285 eV broadened. These spectral changes are ascribable to the change from σ(C–C) to σ(C–Si) and an increase in the composition ratio of C=C–Si sites with the Si/(C+Si) ratio in the Si-DLC films. However, the spectral feature of the Si K-edge NEXAFS spectra of the Si-DLC films did not significantly change along with the Si/(C + Si) ratio. This is considered due to the fact that the Si atom positioned between C atoms in Si-DLC films and/or the chemical environment of an Si atom does not change much between Si–C and Si–Si bonding. Namely, the electronic state of Si in the Si-DLC film is not affected by the Si/(C + Si) ratio.

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