Title: Structural Analysis of a-C:H and a-C:H:Si Films under High-Pressure and High-Temperature by Synchrotron X-Ray Diffraction

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Abstract:

Amorphous carbon films have several outstanding tribology characteristics, including high hardness, surface smoothness, and low friction. Under tribological conditions, their surface is generally exposed to high-temperature and pressure. Although the structure of amorphous carbon films is likely changed by high temperature and pressure, there have been no reports on such structural changes of the films. To obtain information about their structural changes, synchrotron X-ray diffraction was used to analyze two kinds of amorphous carbon films, a-C:H and a-C:H:Si, under high-temperature and high-hydrostatic pressure conditions. Synchrotron X-ray diffraction was applied to films pressurized by a multi-anvil press installed in the PF-AR NE5C beamline at KEK at room temperature and at a high-temperature around 200°C. The pair distribution functions derived by Fourier transformation of the obtained scattering intensity profiles showed that the sp^2/sp^3 ratios for both films decreased as the pressure increased and that the sp^2/sp^3 ratio for the a-C:H film increased as the

temperature increased. This indicates that high-pressure creates sp^3 stabilization in a-C:H and a-C:H:Si films while high-temperature creates sp^2 transition in a-C:H film. The sp^2/sp^3 ratio for the a-C:H:Si film did not change much even at high-temperature due to the high thermal-oxidative stability of a-C:H:Si.

Keywords:

a-C:H, a-C:H:Si, Structural analysis, Synchrotron X-ray diffraction, High temperature, High pressure, Pair distribution function, sp^2/sp^3 ratio

Body of Paper:

1. Introduction

Amorphous carbon films have several outstanding characteristics including high hardness, surface smoothness, low friction, and high wear durability. They are commonly called ‘diamond-like carbon (DLC) films’, especially in industrial field of mechanical engineering¹⁻⁴), and are widely used in cutting tools^{5,6}), bearings⁷⁻⁹), magnetic recording disks and heads¹⁰⁻¹⁴), microelectromechanical systems (MEMS)¹⁵⁻¹⁸), and various other applications¹⁹⁻²²). The use of amorphous carbon films in automotive parts, such as engines²³⁻²⁷), valve lifters²⁸⁻³⁰), and clutches³¹), has particularly received considerable attention, and research has shown that vehicles with parts made using such films have much better fuel economy than ones that do not.

Amorphous carbon films generally consist of two kinds of carbon bonds; the sp^2 bonds found in graphite and the sp^3 bonds found in diamond^{32,33}). The hardness of amorphous carbon film is higher when the film has a smaller volume of hydrogen atoms and a larger volume of sp^3 bonds. There are many types of amorphous carbon films on the market, and their properties depend on the deposition method, conditions, and apparatus used to make them. This means that users can choose the type that best meets their requirements. Metal doping of amorphous carbon films is possible, and various kinds of elements have already been used for such doping to further improve the properties³⁴⁻³⁷). Silicon-doped amorphous carbon films, for example, are better than undoped films in terms of thermal oxidative stability³⁸⁻⁴³).

Films used under tribological conditions for lower friction coefficient and higher wear durability are subjected to high-pressure and high-temperature due to friction heat at the contact points. Their carbon structure is sensitive and changes due to pressure and heat, resulting in a change in their tribological properties. In spite of the importance of this for estimating film performance and lifetime, there have been few reports on the changes in carbon structure in amorphous carbon films^{1,32,33,44}).

Various methods have been proposed and developed for structural analysis of amorphous carbon films. Raman spectroscopy is the most common method. It can provide information on the sp^2/sp^3 ratio from the peak intensities at the corresponding wave-lengths for sp^2 and sp^3 bonds^{1,33}). Elastic recoil detection analysis (ERDA) provides an accurate existence percentage for hydrogen atoms in films, and the hydrogen atom contents for various films have been quantified⁴⁵). X-ray diffraction (XRD) is not so major for such film analysis, but the residual stress in films has been quantified in the past studies^{1,46-48}). XRD is excellent for quantitative analysis of bonding structures because it enables the number of sp^2 and sp^3 bonds to be individually

estimated in principle if the pair distribution functions can be obtained because the atomic distances in sp^2 and sp^3 bonding structures differ.

In the study reported here, we used synchrotron XRD to clarify the pair distribution functions of amorphous carbon films. To apply high-pressure and high-temperature to the films, the films were put into a cubic cell and the cell was set in the synchrotron beamline with multi-anvils. The films used for this first study were undoped and Si-doped hydrogenated amorphous carbon films (a-C:H and a-C:H:Si), selected due to their easy availability and general versatility. The change in the structure of each film due to pressure and heat was investigated by using their pair distribution functions.

2. Theory for Structural Analysis^{49,50)}

A pair distribution function is an existence probability distribution of atoms in a thin sphere shell with distance r from a reference atom. The function expresses the internal structure in amorphous materials with atomic correlations, and is defined as

$$g(r) \equiv \rho(r)/\rho_0 \quad (1)$$

where $\rho(r)$ and ρ_0 are the density distribution corresponding to the existence probability of atoms and the average number density of the material, respectively.

The relationship between scattering intensity $I(Q)$ from the amorphous material and the $g(r)$ of the material is given by

$$I(Q) = I_e N f^2 \left[1 + \int_0^\infty 4\pi r^2 \rho_0 \{g(r) - 1\} \frac{\sin(Q \cdot r)}{Q \cdot r} dr \right] \quad (2)$$

where Q , N , I_e , and f are the scattering vector, the number of atoms contributing to the scattering, the scattering intensity of an electron, and the atomic scattering factor, respectively. Structural factor $S(Q)$ is then defined as $I(Q)$ normalized by the scattering intensity for an ideal material without atomic correlation:

$$S(Q) \equiv \frac{I(Q)}{I_e N f^2} = 1 + \int_0^\infty 4\pi r^2 \rho_0 \{g(r) - 1\} \frac{\sin(Q \cdot r)}{Q \cdot r} dr \quad (3)$$

Fourier transformation of Eq. (3) gives

$$g(r) = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^\infty \{S(Q) - 1\} \frac{\sin(Q \cdot r)}{Q \cdot r} Q^2 dQ \quad (4)$$

After $I(Q)$ is experimentally acquired from diffraction, $S(Q)$ is obtained from Eq. (3), and $g(r)$ is finally obtained by Fourier transformation of $S(Q)$ using Eq. (4).

3. Experiment

3.1 Apparatus

The experiment for structural analysis of amorphous carbon films was carried out the MAX80, multi-anvil press installed in the PF-AR NE-5C beamline of the High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan^{51,52}. The optical alignment in the beamline with a sample cell is shown in Fig. 1. The multi-anvil press has a pair of dies at the top and bottom and six cubic anvils made from cemented carbide are located between the dies, as shown in the figure. When the dies are pressed vertically, the cubic anvils are pressed to the center as well, resulting in the sample cell being pressurized hydrostatically by the six anvil faces. The face size of the anvils we used was 12×12 mm.

In our experiment, synchrotron white X-rays were used. Those passing through the upper slit irradiated the sample cell through the gap between the side anvils. The X-rays diffracted from the sample passed through the gap between the side anvils and a collimator and struck a one-dimensional solid state detector (SSD), which enabled the diffracted beam to be resolved in accordance with its energy (i.e., wave-length). The upper slit was 0.1×0.5 mm on its vertical and horizontal axes, respectively, and the lower slit in front of the detector was 0.1×0.2–2.0 mm. (The horizontal slit length was changed in accordance with the intensity of the diffracted beam.) The hole in the collimator had a diameter of 0.3 mm.

3.2 Composition of Sample Cell

The compositions of the sample cells are shown in Fig. 2. The cell on the left is the one used for the experiment at room temperature, and the one on the right is the one used for the experiment at high temperature.

Two kinds of amorphous carbon films, a-C:H and a-C:H:Si, were deposited onto a polyvinyl alcohol (PVA) sheet to a film thickness of 1 μm by normal chemical vapour deposition (CVD) and plasma-based ion implantation and deposition (PBIID), respectively. The introduced gases for a-C:H and a-C:H:Si were CH₄ and a mixture of C₂H₂ and Si(CH₃)₄, respectively. The resulting films were carefully peeled from the PVA sheet and placed into a capsule (φ6 mm inner diameter, φ8 mm outer diameter, and 5 mm high) made of polytetrafluoroethylene (PTFE) until the capsule was completely full. The capsule was placed in a cube made of boron epoxy resin as a pressure-transmitting medium with high permeability to X-rays. A NaCl plate was placed in the cube with the PTFE capsule for pressure calibration, as shown in Fig. 2.

In the cube for the experiment at high temperature, a 0.2 mm-thick graphite

plate for use a sheet heater, gold strips for use as electrical wiring, and an alumel-chromel wire for use as a thermocouple for temperature measurement were additionally placed, as shown on the right in Fig. 2. The current for heating the graphite plate was input through the cubic anvils at the top and bottom under closed-loop control.

3.3 Conditions

Profiles of the X-ray scattering intensity were acquired at room temperature ($\sim 25^\circ\text{C}$) and high temperature ($\sim 200^\circ\text{C}$) under loading conditions (up to ~ 1.5 GPa) and unloaded conditions. The pressure was estimated on the basis of the shifts in the NaCl intensity peaks.

To obtain the pair distribution functions, X-ray intensity profiles were acquired for 13 angles ($2\theta = 2, 3, 5, 6, 8, 10, 12, 14, 16, 18, 20, 22$, and 25°) until the total count in the detector reached 3000 for each angle. The irradiation duration for acquiring the profile for one angle was about 30–90 minutes.

4. Results and Discussion

4.1 Structural Change in a-C:H Film at Room Temperature

The intensity profiles for a-C:H film at room temperature under ambient pressure are shown in Fig. 3. The horizontal axis shows the energy of the irradiated X-rays. All profiles were broad without sharp peaks because the a-C:H was completely amorphous. The profiles for high pressure, 860 and 1640 MPa, estimated from the shifts in the NaCl intensity peaks, were also broad without sharp peaks.

The pair distribution functions for a-C:H film calculated from Eqs. (3) and (4) are shown in Fig. 4. The horizontal axis shows the atomic distance. The functions had four peaks around $r = 1.46, 2.50, 3.60$, and 4.70 Å corresponding to the major distances between atoms in a-C:H, as shown at the top in Fig. 4. The peak around 1.46 Å corresponds to the closest C-C distances in sp^3 and sp^2 bonding, while the peaks around $2.50, 3.60$, and 4.70 Å correspond to the C-C distances in sp^2 bondings. (The ideal closest C-C distances in sp^3 and sp^2 bondings are 1.54 and 1.42 Å, respectively. Therefore it can be assumed that the peak around 1.46 Å is formed by the additional combination of both peaks.) The distances between C and H atoms were acquired from the pair distribution functions because H is small enough for X-ray scattering. (The ideal C-H distance is 1.10 Å.) The reason the atomic distances with peak in the function were not exactly the same as the ideal C-C distances may be that there were five- or seven-membered rings instead of the typical six-membered rings and/or that there was

some kind of random structure in the amorphous film^{1,53}).

On the basis of the discussion above, we estimated the sp^2/sp^3 ratio, that is, the ratio of graphite structure to diamond structure, from the obtained pair distribution functions. Since the first and second peaks around $r = 1.46$ and $2.50 \text{ \AA}$ correspond to the existence probabilities of sp^3+sp^2 and sp^2 respectively, the sp^2/sp^3 ratio was quantified using the Gaussian-fitted areas for the first and second peaks in the function, a_1 and a_2 , as $a_2/(a_1 - a_2)$. (Weight coefficient k corresponding to the existence probability of atoms with a distance of $1.46 \text{ \AA}$ against that with a distance of $2.50 \text{ \AA}$ in the ideal carbon amorphous structure should be multiplied by a_2 . However, since the value of k is unknown, $k = 1$ is assumed here.)

The sp^2/sp^3 ratio for a-C:H film is shown in Fig. 5. It decreased gradually with an increase in load pressure, meaning that the diamond structure in a-C:H film increased by pressure. The ratio under the unloaded condition after loading returned to its original value, meaning that the sp^2/sp^3 ratio for a-C:H film can be reversibly altered with respect to the load pressure.

4.2 Structural Change in a-C:H Film at High Temperature

The pair distribution functions for a-C:H film at high temperature ($\sim 200^\circ\text{C}$) are shown in Fig. 6. These functions were also derived from the X-ray intensity profiles acquired for 13 angles. Because a light precompression was necessary for the experiment at high temperature to input current to the graphite plate, the functions could not be derived under ambient pressure at 200°C .

The sp^2/sp^3 ratio, estimated as described above, is shown in Fig. 7. It was significantly higher than that at room temperature. This means that the proportion of graphite structure increased in the a-C:H film due to the higher temperature. The ratio decreased slightly as the pressure was increased, as it did in the room-temperature experiment. The ratio under the unloaded condition after loading returned to a value close to the original value, meaning that the sp^2/sp^3 ratio for a-C:H film can be reversibly altered with respect to the load pressure even under high-temperature conditions.

After the high-temperature experiment, the sample cell was gradually cooled down in air, and the intensity profiles were again acquired; the sp^2/sp^3 ratio at room temperature (the final state) is also plotted in Fig. 7. It was much larger than the original value, meaning that the proportion of graphite structure increased despite the temperature reduction. This indicates that the structural change from diamond to graphite proceeded during the air-cooling process. This experiment demonstrated that

the sp^2/sp^3 ratio for a-C:H film can be irreversibly altered with respect to the temperature.

4.3 Structural Change in a-C:H:Si Film at Room Temperature

The intensity profiles for a-C:H:Si film at room temperature under ambient pressure are shown in Fig. 8. All profiles were broad without sharp peaks, like the results for a-C:H film shown in Fig. 3.

The pair distribution functions for a-C:H:Si film at room temperature are shown in Fig. 9. The atomic distances with peak were slightly shifted due to the existence of Si atoms when compared to the functions for a-C:H film (because the pure C-Si distance is 1.88 Å and longer than that of C-C distance in sp^3 bonding, 1.54 Å), shown in Fig. 4; the distances for the first and second peaks were around $r = 1.70$ and 2.90 Å, respectively. However, the first and second peaks are considered to correspond to the existence probabilities of sp^3+sp^2 and sp^2 , respectively, as for the a-C:H film.

The sp^2/sp^3 ratios estimated from the pair distribution functions are shown in Fig. 10. They decreased slightly when the pressure was increased. In addition, the ratio under the unloaded condition after loading did not return to the original value. This indicates that a structure composed of C-Si bonding is irreversible with respect to pressure because the dissociation energy of C-Si bonding is smaller than that of C-C bonding (451 kJ/mol vs. 607 kJ/mol). However, the change in the sp^2/sp^3 ratios for a-C:H:Si film before and after loading was not so clear when compared to the change for a-C:H film before and after a temperature increase.

4.4 Structural Change of a-C:H:Si Film at High Temperature

The pair distribution functions for a-C:H:Si film at high temperature (~200°C) and the sp^2/sp^3 ratios estimated from the pair distribution functions are shown in Figs. 11 and 12, respectively. Fig. 12 shows that the ratios decreased slightly even at high temperature when the pressure was increased. The ratio under the unloaded condition after loading returned to a value close to the original value. The ratio after air-cooling was slightly smaller compared to that before cooling. However, the change in the sp^2/sp^3 ratios for a-C:H:Si film across all experiments was considerably smaller than that for a-C:H film, even at high temperature. While there have been reports that Si-doping into amorphous carbon improves its thermal-oxidative stability, our results showed that the sp^2/sp^3 ratio for a-C:H:Si film does not change much even under high-pressure and high-temperature conditions, meaning that Si-doping makes the structure in amorphous carbon much more stable.

5. Conclusion

The structural changes in a-C:H and a-C:H:Si films due to temperature and pressure were investigated using synchrotron X-ray diffraction.

(1) The scattering intensity profiles for both films had broad peaks without any sharp peaks. The pair distribution functions, which express the existence probabilities of atoms in the amorphous material, were derived by Fourier transformation of the intensity profiles obtained at 13 2 θ angles.

(2) The pair distribution functions showed that the sp²/sp³ ratios for both films decreased as the pressure increased and that the sp²/sp³ ratio for a-C:H film increased as the temperature increased. This indicates that high pressure brings about sp³ stabilization in a-C:H and a-C:H:Si films, while high temperature brings about sp² transition in a-C:H film.

(3) The change in the sp²/sp³ ratios for a-C:H:Si film across all experiments was considerably smaller than that for a-C:H film, even at high temperature. This means that amorphous carbon structure became much more stable due to the Si-doping.

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Nomenclature

a_1 : Gaussian-fitted areas of first peaks in $g(r)$

a_2 : Gaussian-fitted areas of second peaks in $g(r)$

f : Atomic scattering factor

$g(r)$: Pair distribution function

r : Distance from reference atom

I_e : Scattering intensity of an electron

$I(Q)$: Scattering intensity

N : Number of atoms contributing for the scattering

Q : Scattering vector

ρ_0 : Average number density of the target material

$\rho(r)$: Density distribution corresponding to existence probability of atoms

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Figure Captions

- Fig. 1 Optical alignment in MAX80 multi-anvil press installed in PF-AR NE-5C beamline
- Fig. 2 Compositions of cubic sample cells (left: for experiment at room temperature, right: for experiment at high temperature)
- Fig. 3 XRD intensity profiles for a-C:H film at room temperature for 13 2θ angles
- Fig. 4 Pair distribution functions for a-C:H film at room temperature
- Fig. 5 sp^2/sp^3 ratio for a-C:H film at room temperature
- Fig. 6 Pair distribution functions for a-C:H at $\sim 200^\circ\text{C}$
- Fig. 7 sp^2/sp^3 ratio for a-C:H at $\sim 200^\circ\text{C}$
- Fig. 8 XRD intensity profiles for a-C:H:Si film at room temperature for 13 2θ angles
- Fig. 9 Pair distribution functions for a-C:H:Si film at room temperature
- Fig. 10 sp^2/sp^3 ratio for a-C:H:Si film at room temperature
- Fig. 11 Pair distribution functions for a-C:H:Si film at $\sim 200^\circ\text{C}$
- Fig. 12 sp^2/sp^3 ratio for a-C:H:Si film at $\sim 200^\circ\text{C}$

Fig. 1 Optical alignment in MAX80 multi-anvil press installed in PF-AR NE-5C beamline

Fig. 2 Compositions of cubic sample cells (left: for experiment at room temperature, right: for experiment at high temperature)

16

Fig. 4 Pair distribution functions for a-C:H film at room temperature

Fig. 5 sp^2/sp^3 ratio for a-C:H film at room temperature

Fig. 6 Pair distribution functions for a-C:H at $\sim 200^\circ\text{C}$

Fig. 7 sp^2/sp^3 ratio for a-C:H at $\sim 200^\circ\text{C}$

19

Fig. 9 Pair distribution functions for a-C:H:Si film at room temperature

Fig. 10 sp^2/sp^3 ratio for a-C:H:Si film at room temperature

Fig. 11 Pair distribution functions for a-C:H:Si film at ~200°C

Fig. 12 sp^2/sp^3 ratio for a-C:H:Si film at ~200°C