Self-supporting tetrahedral amorphous carbon films consisting of multilayered structure prepared using filtered arc deposition

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ARTICLE INFO
Keywords:
Diamond-like carbon
Tetrahedral amorphous carbon
Multilayer film
Self-supporting film
Carbon film target
Laser-driven ion acceleration
Laser irradiation tolerance

ABSTRACT
Self-supporting 110-nm-thick tetrahedral amorphous carbon (ta-C) films with a multilayered structure were fabricated as a carbon film target for the laser-driven ion acceleration. The self-supporting ta-C films consisted of three layers with the thicknesses of 35 nm, 40 nm, and 35 nm thick, and the film density of 3.0 g/cm³, 2.7 g/cm³, and 3.0 g/cm³, respectively. The multilayered ta-C film was fabricated using the T-shape filtered arc deposition method on a Si substrate coated with a water-soluble material. Silk fibroin and dextran were used as the water-soluble material. The water-soluble material formed between a ta-C film and a Si substrate was dissolved, and then, the ta-C film released from the substrate. Thick single-layer ta-C films partially peeled off on the water-soluble material and broke during the dissolving process. Self-supporting ta-C films were obtained by scooping the released ta-C film on a perforated substrate. The laser was irradiated on the self-supporting ta-C films, and the ta-C film with a higher film thickness and/or film density showed a higher laser irradiation tolerance.

1. Introduction
A laser-driven ion accelerator has been expected as a small-size ion accelerator. In the laser-driven ion acceleration method, high-energy ions originated from thin film elements can be obtained by irradiating a high-intensity short-pulse laser to a thin film target [1–7]. The thin film target used for the laser-driven ion acceleration needs to be a self-supporting thin film without a supporting substrate. One of the uses of high-energy ions is heavy-particle radiotherapy for cancer treatment. Carbon ions are used for heavy-particle radiotherapy.

One candidate for a carbon thin film target material is a diamond-like carbon (DLC) film [8,9]. DLC films are amorphous carbon films in which the sp² and sp³ structures of carbon are mixed, and it is divided into four main groups based on the sp³ ratio and hydrogen content [10,11]. A tetrahedral amorphous carbon (ta-C) film is a DLC film with a high film density owing to a high sp³-ratio and hydrogen-free film. Smooth ta-C films with a high film density can be fabricated by using the filtered arc deposition method [11–18]. However, in the film formation process of DLC films that are an amorphous structure, a base substrate is necessary. Therefore, to obtain a self-supporting DLC film, the DLC film must be released from the substrate after its formation. Furthermore, as the film thickness and film density of a DLC film increase, the internal stress of the DLC film increases. An increase in the internal stress of a DLC film leads to its breakage before the self-supporting process.

As a self-supporting method of a DLC film formed on a substrate, there are a method of dissolving the substrate [19,20] and a method of dissolving a sacrificial layer that is formed between a substrate and a DLC film [21,22]. A DLC film with a thickness of 100 nm is formed on a solid soap by using the pulsed laser deposition (PLD) method, and the DLC film is released by dissolving the soap [19]. In the case of NaCl substrates or sacrificial layers, DLC films are prepared on NaCl by sputtering, PLD, and filtered arc deposition [9,20–22]. When a NaCl layer as a sacrificial layer is formed on a substrate by the vacuum vapor deposition method, the NaCl layer becomes a polycrystalline layer, and the surface roughness of the NaCl layer is transferred to the DLC film [21]. In our previous study, several materials were used as sacrificial layers or substrates in the preparation of self-supporting gold-sputtered...
thin films [23]. A NaCl film formed by the vacuum vapor deposition and a silk fibroin film formed by the spin coating method were used as the sacrificial layers. Silk fibroin is a natural protein constituting cellulose together with sercin [24]. When the NaCl sacrificial layer was used, the roughness of the polycrystalline NaCl surface was transferred to the gold thin film. The surface of the silk fibroin sacrificial layer was not smooth because aggregated silk fibroin existed in the sacrificial layer.

In this paper, the fabrication of self-supporting ta-C film with low hydrogen content and high film density is presented. In addition, self-supporting DLC films with different thicknesses and densities were prepared, and the difference in tolerance to laser irradiation was evaluated. Fig. 1 shows the fabrication flow of self-supporting films by using a sacrificial layer. A sacrificial layer is formed on a base substrate and an objective film is deposited on that sacrificial layer. The prepared substrate is immersed in a solvent, which results in the sacrificial layer being dissolved and the film released from the base substrate. The film floating on the solvent surface is scooped onto a porous substrate. Self-supporting films are formed by covering the holes of the porous substrate.

2. Experimental procedure

2.1. Preparation of sacrificial layers

First, sacrificial layers were formed on glass substrates. Silk fibroin and dextran [25] were used as water-soluble sacrificial layers owing to their low environmental load. Silk fibroin solution with a concentration of 10 wt% was obtained by adding silk fibroin powder (Matsuda silk farm Nanofibroin powder) to purified water, and the silk fibroin solution was filtered through two filters for removing agglutinated particles and contaminations before the spin coating process. A metal, with a pore diameter of 125 mm, and a membrane, with a pore diameter of 0.22 mm, were used as filters. The silk fibroin solution of 300 μl was dropped at on a glass substrate. The glass substrate was rotated for 30 s at 300 rpm by the spin coater (Mikasa Spinner IH-D3), and additionally for 30 s at 2000 rpm.

Dextran is a polysaccharide that is less likely to agglomerate during the solution preparation. In addition, dextran solution takes a longer time to rot than silk fibroin solution. Dextran powder (Tokyo chemical industry Dextran 40) was dissolved in purified water to prepare a dextran solution with a concentration of 5 wt%. The dextran solution of 500 μl was dropped at on a glass substrate. A dextran sacrificial layer was prepared by rotating the glass substrate for 10 s at 300 rpm using the spin coater and additionally for 30 s at 2000 rpm.

2.2. Fabrication of single-layer and multilayer ta-C films

DLC films were fabricated onto sacrificial layers on glass substrates using the T-shape filtered arc deposition [11,15,17,18]. An annular mask was placed on a substrate in the DLC deposition process. The substrates were fixed to the substrate holder using carbon double-stick tapes. Graphite was used as the cathode material, and the arc current was set at 30 A. The base pressure of a chamber was less than 10⁻⁸ Pa by vacuumed using a rotary pump equipped a mechanical booster pump through a turbo molecular pump. Thickness and other properties of DLC films were varied by controlling the deposition duration and substrate-bias voltage, respectively.

Single-layer DLC films were deposited on the silk fibroin and dextran sacrificial layers with a pulse substrate-bias voltage of −100 V. In addition, single-layer DLC films were deposited on the dextran sacrificial layers with a pulse substrate-bias voltage of −800 V. The film densities of DLC films formed at pulse substrate-bias voltages of −100 V and −800 V were approximately 3.1 g/cm³ and 2.7 g/cm³, respectively [11]. A multilayer DLC film was prepared by laminating three layers of DLC films with different film densities on the dextran sacrificial layer. A DLC film was deposited at a pulse substrate-bias voltage of −300 V (the DLC film density of 3.0 g/cm³) on the sacrificial layer, and then a DLC film with a pulse substrate-bias voltage of −800 V was deposited. Further, a DLC film was formed as the top layer at a pulse substrate-bias voltage of −300 V, and the total film thickness was 110 nm (35 nm / 40 nm / 35 nm).

2.3. Sacrificial layer dissolution and ta-C scoop-up processes

After the DLC films were prepared on the substrate-coated sacrificial layers, the substrates were immersed in purified water. The DLC films released from the substrates because the sacrificial layer dissolved in the purified water. The released DLC films were scooped on the perforated substrates (size 50 × 50 × 1 mm³, hole diameter 1 mm, made of stainless steel). The perforated substrates were polished in alcohol using an ultrasonic bath before they were used because the surfaces had been contaminated with oil.

2.4. Evaluation of laser irradiation tolerance

Our assumed irradiation laser for the laser-driven ion acceleration is the high-intensity short-pulse laser (J-KAREN, laser wavelength of 800 nm, pulse width of 40 fs, laser intensity of 10²² W/cm², spot diameter of 3 μm) at the Kansai Photon Science Institute of the National Institutes for Quantum and Radiological Science and Technology in Japan [1–3]. When this high-intensity short-pulse laser was used, it is considered that the film thickness suitable for the thin film target is about 110 nm. During the laser irradiation using the high-intensity short-pulse laser, the prepulses reach the film target before the main pulse that is used for the ion acceleration [5,7]. The intensity of the prepulse is approximately 10 orders of magnitude lower than that of the main pulse. When the thin film is destroyed by the prepulse, ion acceleration by the main pulse does not occur. Therefore, it is necessary for the film target to exhibit tolerance to the prepulse irradiation. To evaluate the tolerance to laser irradiation, laser irradiation tests were conducted on the self-supporting films by using a semiconductor laser. The laser wavelength was 785 nm, and the laser spot diameter was 1 μm. The laser irradiation duration was 1 ms. After laser irradiation, the films were observed using an optical microscope.

3. Results and discussion

3.1. Fabrication of self-supporting single-layer ta-C films by dissolving silk fibroin sacrificial layer

Table 1 shows the optical microscope images of single-layer ta-C films formed on the 300-nm-thick silk fibroin sacrificial layers. For the ta-C films, the \( \frac{I_D}{I_G} \) ratio of 0.36 was obtained by Raman spectroscopy. A ta-C
film had a film density of 3.1 g/cm³; at a thickness of 15 nm, the film was a smooth surface. At a film thickness of 25 nm, mesh patterns appeared in the ta-C film. Fine mesh patterns were observed with an increase in the film thickness. The mesh patterns that appeared in the ta-C film on the sacrificial layer were observed using a scanning electron microscope as shown in Fig. 2. The ta-C film peeled from the sacrificial layer in a wave pattern. From Fig. 2(b), it was found that the sacrificial layer remained on the substrate, while the ta-C film peeled from the sacrificial layer. There were spaces between the ta-C film and the sacrificial layer. The DLC films peel off in wave-like patterns when the adhesion between the underlayer and DLC is low [15, 26, 27]. The film density of the DLC was 3.1 g/cm³, which is high [11]. The adhesion between the soft silk fibroin sacrificial layer and the hard ta-C film is low. It was assumed that the thick ta-C films peeled from the silk fibroin sacrificial layers with low adhesion because the internal stress of the ta-C film increased as the ta-C film with a high film density becomes a thick film.

The sacrificial layer under the 110-nm-thick ta-C film with mesh patterns was dissolved, and the ta-C film floating on the water surface was scooped on a porous substrate, as shown in Fig. 3. The part of the ta-C films on the holes in the porous substrate broke. As shown in Fig. 3(b), the ta-C film remaining on the hole had large wrinkles and cracks.

The self-supporting process was also performed on a 15-nm-thick ta-C film without a mesh pattern. Fig. 4 shows the ta-C film with a film thickness of 15 nm scooped on a porous substrate. Self-supporting ta-C films were formed on a significant number of holes in the porous substrate as shown in Fig. 4(a). From Fig. 4(b), it can be observed that the self-supporting ta-C film was smooth and flat without wrinkles and cracks. Peelings in a ta-C film cause film distortion such as mesh patterns. It was considered that the film distortion was weak to the external stress during the releasing and scoop-up processes and led to breakage of the whole film.

**Table 1**

Optical micrograph images of the surfaces of single-layer ta-C films on silk fibroin sacrificial layer.

<table>
<thead>
<tr>
<th>ta-C film density</th>
<th>ta-C film thickness</th>
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<tr>
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</tr>
<tr>
<td></td>
<td>25 nm</td>
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<td></td>
<td>110 nm</td>
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![Fig. 2](image1.png)

**Fig. 2.** (a) Top-view and (b) cross-sectional SEM images of local detachment of DLC film on silk fibroin sacrificial layer.

![Fig. 3](image2.png)

**Fig. 3.** (a) Photographs of single-layer 110-nm-thick ta-C film on perforated substrate and (b) its magnified view.

![Fig. 4](image3.png)

**Fig. 4.** (a) Photographs of single-layer 15-nm-thick ta-C film on perforated substrate and (b) self-supporting 15-nm-thick ta-C film.
3.2. Fabrication of self-supporting single-layer and multilayer ta-C films by dissolving dextran sacrificial layer

Table 2 shows the optical microscope images of a single-layer ta-C film formed on 70-nm-thick dextran sacrificial layer. Similar to the silk fibroin sacrificial layer, mesh patterns appeared in the dextran sacrificial layer with an increase in the film thickness of ta-C films with a film density of 3.1 g/cm$^3$. On the other hand, in ta-C films with a film density of 2.7 g/cm$^3$, even if the film thickness was increased to 110 nm, which was the target film thickness of the self-supporting film, mesh patterns did not appear.

Considering the relationship between the film thickness and the film density capable of forming a single-layer film without peeling on a sacrificial layer, a multilayer ta-C film consisting of ta-C films with film densities of 3.0 g/cm$^3$ and 2.7 g/cm$^3$ was prepared on a dextran sacrificial layer. Fig. 5(a) shows an optical microscope image of a multilayer 110-nm-thick ta-C film on the dextran sacrificial layer. The multilayer ta-C film was flat and had no mesh pattern. Self-supporting multilayer ta-C films obtained by dissolving the sacrificial layer and scooped up on a porous substrate are shown in Fig. 5(b) and (c). The multilayer ta-C film maintained a flat shape on a hole and did not have any wrinkles and cracks, as shown in Fig. 5(c). The internal stress of the thick ta-C film was relaxed by changing its density, and it was assumed that ta-C film did not peel even if the film thickness increased. The thick ta-C film did not break in the self-supporting process because the ta-C film had no peelings on the sacrificial layer.

![Table 2](image)

<table>
<thead>
<tr>
<th>ta-C film density</th>
<th>ta-C film thickness</th>
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<tbody>
<tr>
<td>3.1 g/cm$^3$</td>
<td>20 nm 40 nm 110 nm</td>
</tr>
<tr>
<td></td>
<td>200 µm 200 µm 200 µm</td>
</tr>
<tr>
<td>2.7 g/cm$^3$</td>
<td>200 µm 200 µm 200 µm</td>
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</table>

Fig. 5. Multilayer 110-nm-thick ta-C film. (a) Optical micrograph images on dextran sacrificial layer. (b) Photographs on perforated substrate. (c) Self-supporting 110-nm-thick ta-C film.

3.3. Laser irradiation tolerance of self-supporting ta-C films

Fig. 6 shows the results of the laser irradiation on the self-supporting multilayer ta-C film with varying laser intensity. As shown in Fig. 6(a), no laser irradiation mark was observed on the multilayer ta-C film after laser irradiation at the intensity of $1.2 \times 10^3$ J/cm$^2$. Because the intensity of the prepulses of the assumed laser is approximately $1.0 \times 10^3$ J/cm$^2$, the multilayer ta-C film was considered to have sufficient tolerance to the prepulses. At the laser irradiation intensity of $2.2 \times 10^3$ J/cm$^2$, laser irradiation mark appeared on the multilayer ta-C film, as shown in Fig. 6(b). The tolerance results of the self-supporting

![Fig. 6](image)
ta-C films to laser irradiation are summarized in Fig. 7. The circles indicate that a laser irradiation mark was not observed on a self-supporting ta-C film after laser irradiation, and the crosses indicate that a laser irradiation mark was observed. When the film thickness of ta-C films was equal, the film with the higher density showed a higher laser irradiation tolerance. When the ta-C films had equal densities, the thicker ta-C film had better laser irradiation tolerance. In this study, because the laser intensity could not be divided finely, there was no difference in the laser irradiation tolerance of the single-layer films and the multilayer film. However, a ta-C film with a high film density and a thick film showed better laser irradiation tolerance. Thus, it was considered that the multilayer 110-nm-thick ta-C film had the best laser tolerance among the ta-C films studied.

4. Conclusions

Self-supporting single-layer and multilayer ta-C films were fabricated by using the sacrificial layer dissolution method. In ta-C films with a high density of 3.1 g/cm³, only self-supporting 15-nm-thick ta-C films were obtained. The self-supporting multilayer ta-C films with a film thickness of 110 nm that is target film thickness as the film target for the laser-driven acceleration were obtained by considering the film thickness that can be formed as self-supporting single-layer film. In the laser irradiation test of self-supporting ta-C films, high laser irradiation tolerance was shown with increasing film thickness and/or the film density of the DLC films. We have established a method for fabricating self-supporting DLC films with high film density, and we proposed laminating DLC films with different film densities for film thickness control of the self-supporting films.

Acknowledgments

This work was supported by the JSPS KAKENHI Grant-in-Aid for Scientific Research, Toukai Foundation for Technology, Osaka Scientific Studies Grants Foundation, The Foundation for Technology Promotion of Electronic Circuit Board, the Naito Science and Engineering Foundation, and Tatematsu Foundation.

References