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2016 Jpn. J. Appl. Phys. 55 07LE05

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Preparation of self-supporting Au thin films on perforated substrate by releasing from water-soluble sacrificial layer

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Received November 27, 2015; revised February 19, 2016; accepted March 13, 2016; published online June 15, 2016

A self-supporting thin film is useful as a target material for laser-driven ion acceleration experiments. In this study, 100-nm-thick sputtered gold (Au) thin films were released from substrates using water-soluble sacrificial layers, and the released films were subsequently scooped up on perforated substrates. Au thin films were deposited by DC plasma sputtering on the sacrificial layers. In the releasing test, sodium chloride (NaCl) was shown to be most suitable as a sacrificial layer for Au thin films. In addition, sputtered Au thin films with thicknesses of 50 and 150 nm were deposited onto NaCl sacrificial layers, released on water, and scooped up on perforated substrates. Self-supporting Au thin films were obtained for all film thicknesses, but wrinkles and cracks appeared in the 50 nm film. © 2016 The Japan Society of Applied Physics

1. Introduction

Self-supporting thin films made of diamond-like carbon (DLC)^{1–3)} and gold (Au) have attracted increasing attention as film targets for laser-driven ion acceleration experiments.^{4–8)} One of the methods of manufacturing self-supporting thin films is to use a soluble sacrificial layer.

A thin film can be released from a substrate by dissolving the substrate. Usually, a powerful acid is required for dissolving a typical substrate, such as metal (copper, tungsten, and nanostrands) and silicon (Si).^{9–13)} However, the use of strong acids is unfavorable for industrial production processes. One of the good approaches to avoid this process is to use a sacrificial layer between a typical substrate and the objective film. The objective film is released from the substrate by removing the sacrificial layer. Water-soluble materials, such as sodium chloride (NaCl), nickel chloride, and betaine, were used as the sacrificial layers.^{14–25)} The releasing process of the thin film using a water-soluble material as a sacrificial layer is considered to be safer for humans and the environment than methods using a strong acid with the exception of nickel chloride, which is a carcinogenic material.²⁶⁾

Gold leaf is a self-supporting Au film; however, it is too rough and insufficiently pure to be a suitable target for laser-driven ion acceleration experiments.

The plasma sputtering method²⁷⁾ has been widely used in industry for forming thin films. By this method, the control of film thickness is relatively easy, and the purity of the film material is high. High-purity and flat Au thin films with a thickness of several tenths of nanometers thinner than gold leaf films can be obtained on a substrate by the sputtering method.

In this paper, the releasing and self-supporting processes of Au thin films using a water-soluble sacrificial layer are presented. 100-nm-thick Au thin films were deposited by the plasma sputtering method on substrates possessing a variety of sacrificial layers. The release of the Au thin films from the substrates was attempted by removing the sacrificial layer. Self-supporting Au thin films were then fabricated by transferring the released Au thin films onto perforated substrates.

Gelatin, oblate, silk fibroin, and NaCl were used as water-soluble sacrificial layers owing to their low environmental load. Gelatin²⁸⁾ and oblate are water-soluble materials derived from collagen and made from gelatinized starch, respectively. Silk fibroin is a natural protein composed of raw silk with sericin.²⁹⁾

2. Experimental methods

Gelatin, which becomes a thick film through drying, was used as a sacrificial substrate functioning as a sacrificial layer and a supporting substrate. The gelatin thick film was fabricated as follows: (1) gelatin granules (cooked gelatin, Morinaga) were mixed with purified water at a ratio of 2 : 1, (2) the mixed gelatin solution was cooled at 5 °C for 12 h in a refrigerator, and (3) the clotted gelatin solid was dried at room temperature for 24 h.

Oblates were used as sacrificial substrates in the case of the gelatin substrate. Two different manufacturers' oblates (produced by Niigata Oblate and Takigawa Oblate) were used.

A silk fibroin sacrificial layer was coated onto a glass substrate by a spin coater (Mikasa Spinner IH-D3) after dissolving in purified water at a concentration of 10 wt %. The silk fibroin solution was obtained by maintaining it at 5 °C for 30 min in a refrigerator without stirring after the addition of the silk fibroin powder (Matsuda Silk Farm) to purified water. The silk fibroin solution was set at 300 μl on a glass substrate. The glass substrate was rotated by the spin coater for 30 s at 300 rpm and additionally for 30 s at 2000 rpm.

The NaCl sacrificial layers were deposited onto Si substrates using a vacuum vapor deposition system (Ulvac VPC-260F). NaCl powder was heated to 1000 °C by resistive heating on an evaporation boat. The deposition duration of NaCl was 5 s.

Au thin films were deposited on sacrificial substrates and layers by a DC sputtering system (Sanyu Electron SC-701) as shown in Fig. 1. An annular mask was placed on a substrate in the sputtering process. The distance between a target and a substrate was 25 mm. A pure Au target (99.99%) with a size of φ49 mm × t0.05 mm was used as the sputtering target. The chamber was vacuumed using a rotary pump. The discharge current was 2.5 mA and the atmosphere gas was air during

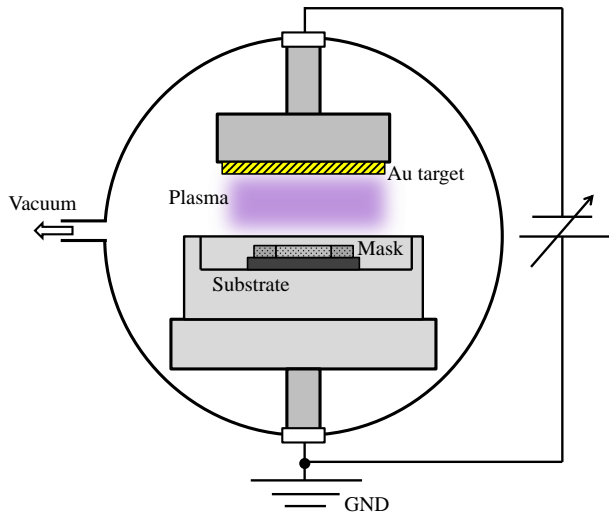


Fig. 1. (Color online) Schematic diagram of the DC sputtering system.

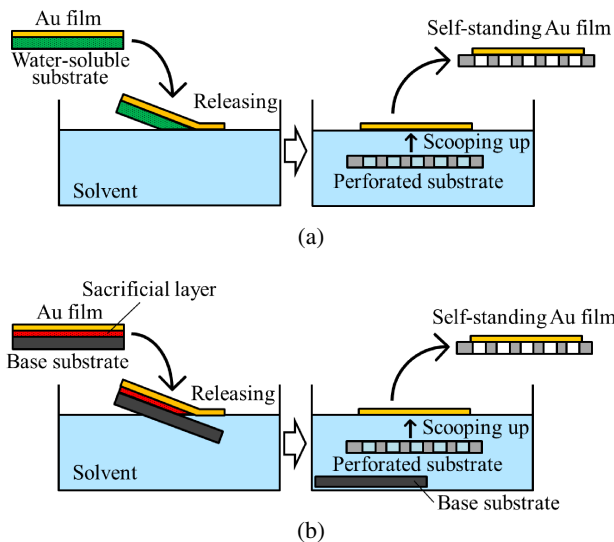


Fig. 2. (Color online) Releasing and self-supporting processes of Au thin film. (a) Sacrificial substrate method. (b) Sacrificial layer method.

the sputtering. The deposition rate and diameter of the Au thin films were 5 nm/min and 35 mm without the mask, respectively. The film thicknesses of the sputtered Au were varied by controlling the deposition duration. The thickness of the Au thin films on gelatin, oblate, and silk fibroin was fixed at 100 nm. The thicknesses of Au thin films on NaCl were 50, 100, and 150 nm.

The substrates with deposited Au thin films were immersed in purified water. Figure 2 shows the releasing and self-supporting processes of Au thin films using sacrificial substrates (gelatin, oblate) and layers (silk fibroin, NaCl). The base substrates were glass and Si substrates in Fig. 2(b). The Au thin films released from the substrates by dissolving the sacrificial substrate or layer in the purified water were scooped up on perforated substrates (size $50 \times 50 \times 1 \text{ mm}^3$, hole diameter 2 mm, aperture ratio 40.2%, made of stainless steel). The perforated substrates were polished in alcohol using an ultrasonic bath before use as a substrate because the surfaces had been contaminated with oil. The Au thin films on the perforated substrates were then dried for 3 h at room

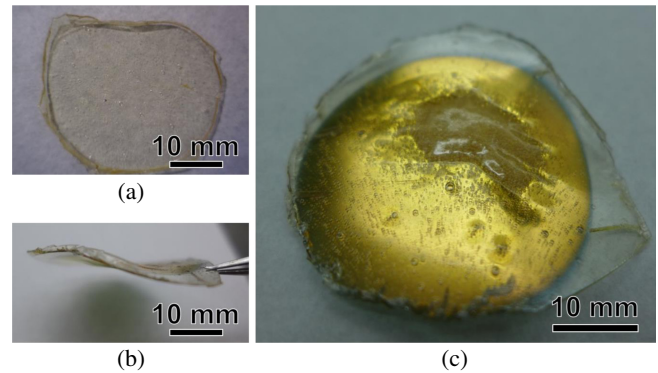


Fig. 3. (Color online) (a) Top- and (b) side-view photographs of the gelatin substrate. (c) Photograph of sputtered Au thin film on the gelatin substrate.

temperature in air atmosphere. The surfaces of silk fibroin, NaCl layers, and Au films were observed by scanning electron microscopy (SEM).

3. Results and discussion

As shown in Figs. 3(a) and 3(b), the fabricated gelatin substrate was not flat because a long time was required to solidify the gelatin solution. When a Au thin film was deposited on the curved gelatin substrate, bubbles appeared in the Au thin film as shown in Fig. 3(c). The bubbles appeared because of the air remaining inside the gelatin substrate.

Figure 4(a) shows photographs of oblate films used as a substrate. The Au film detachment and air bubble formation were not found on the oblate film substrates with deposited Au film as shown in Fig. 4(b). Figure 4(c) shows the appearances of the oblate film substrates with the deposited Au film, at the time when the oblate film substrates were placed in purified water, viewed from the side. Figure 5 shows the illustration of the oblate form change in the water under the same condition as in Fig. 4(c). The Au thin films were not released from the oblate film substrates during the immersion in the purified water because the oblate film substrates did not dissolve in water. The Au films adhered to the oblate films, which were sticky owing to the absorption of water.

When silk fibroin was used as a sacrificial layer, a 100-nm-thick Au thin film was released from the glass substrate by immersing the specimen in purified water, and it was scooped up on a perforated substrate. Figure 6 shows the photographs taken at each step of the process using the silk fibroin sacrificial layer.

Figure 7 shows the SEM images of the specimen surface at each step of the process using the silk fibroin sacrificial layer. Some small humps, several microns in diameter, were observed on the surface of the silk fibroin sacrificial layer in Fig. 7(a). The small humps were also found on the released and self-supporting Au thin films as shown in Figs. 7(b) and 7(c), respectively. The small humps on the silk fibroin sacrificial layer in Fig. 7(a) would be particles made from silk fibroin. The silk fibroin sacrificial layer was made from a silk fibroin solution of dissolved silk fibroin powder in purified water. A part of the silk fibroin powder would become particles because the silk fibroin powder did not dissolve completely in the purified water. Pre-existing contamination

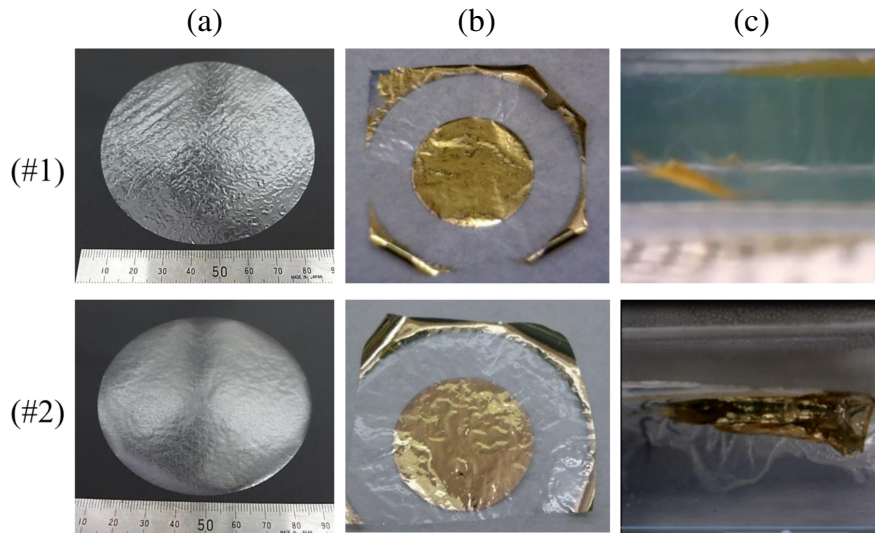


Fig. 4. (Color online) Photographs of (a) as-received oblate films, (b) sputtered Au thin films on the oblate films, and (c) Au thin films with oblate films on water. The oblate manufacturers are (#1) Niigata Oblate and (#2) Takigawa Oblate.

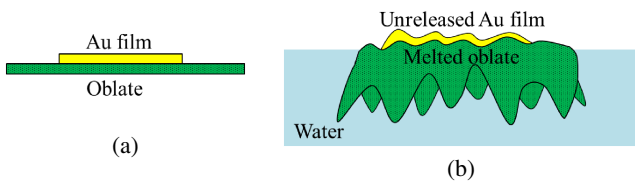


Fig. 5. (Color online) Illustration of oblate film formations (a) before and (b) after being placed in purified water.

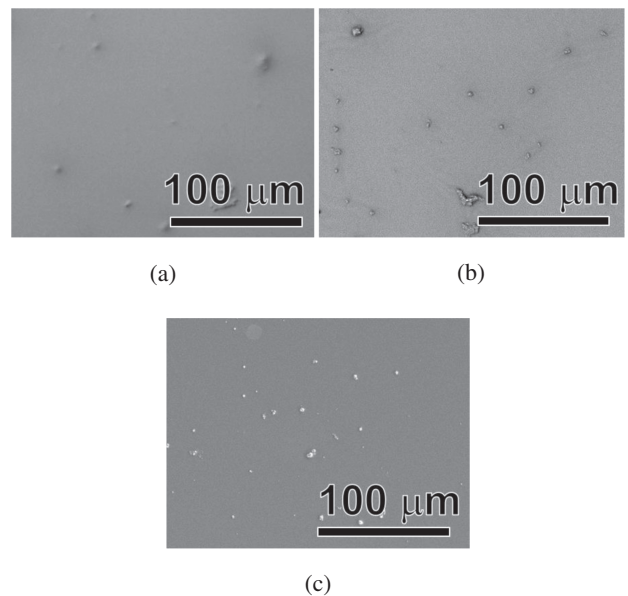


Fig. 7. SEM images of the surfaces of (a) coated silk fibroin sacrificial layer on glass substrate, (b) sputtered Au thin film on silk fibroin sacrificial layer, and (c) self-supporting Au thin film on the apertures of perforated substrate.

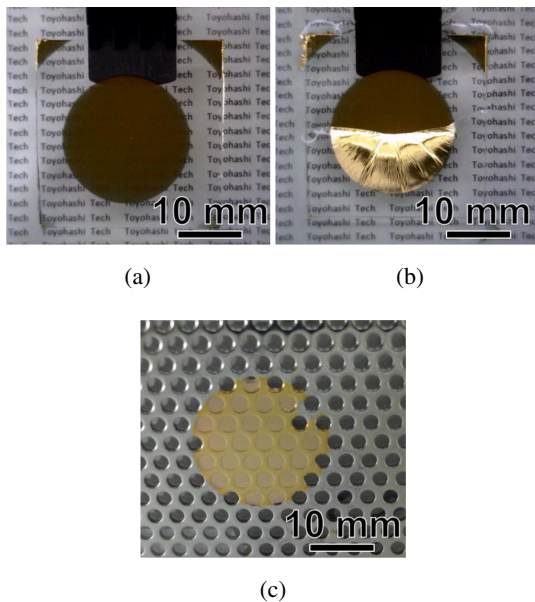


Fig. 6. (Color online) Photographs of the 100-nm-thick Au thin film (a) before releasing from glass substrate, (b) on releasing from the substrate, and (c) after scooping up on perforated substrate using silk fibroin sacrificial layer.

particles on the glass substrate surface could also be the small humps. The small humps in Figs. 7(b) and 7(c) would appear owing to the transfer of the silk fibroin surface geometry to the Au thin film.

When NaCl was used as a sacrificial layer, a 100-nm-thick Au thin film was released from the Si substrate by immersing

the specimen in purified water, where it was scooped up on the perforated substrate. Figures 8(a)–8(c) show photographs taken at each step of the process using the NaCl sacrificial layer. As shown in Fig. 8(c), 70 self-supporting Au thin films of 2 nm diameter on the apertures of the perforated substrate were obtained in the fabrication region of the self-supporting films. The typical self-supporting Au thin film is shown in Fig. 8(d). It was confirmed that the self-supporting Au thin films formed from the released Au thin film were obtained without wrinkles and cracks.

Figure 9 shows SEM images of the specimen surface at each step of the process using the NaCl sacrificial layer. In Fig. 9(a), it was found that NaCl crystal particles were deposited closely in high density on the Si substrate. The diameters of the NaCl particles ranged from 100 to 300 nm. The sizes of the NaCl particles were smaller than the humps

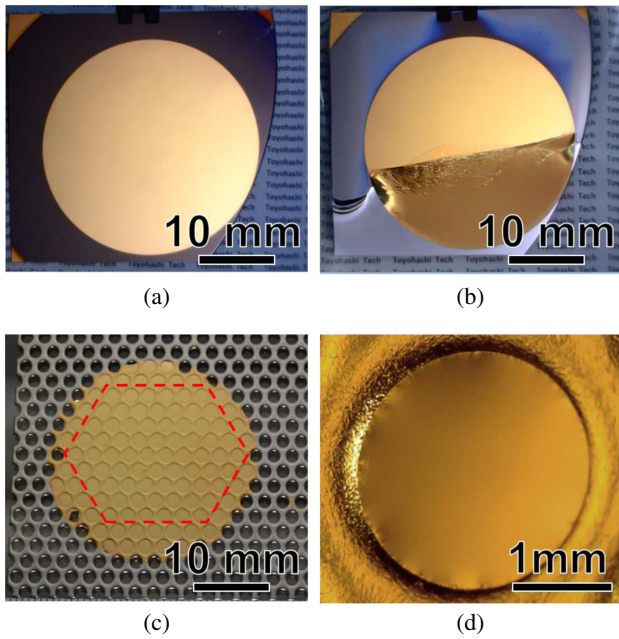


Fig. 8. (Color online) Photographs of 100-nm-thick Au thin film (a) before releasing from glass substrate, (b) on releasing from glass substrate, and (c) after scooping up on perforated substrate using NaCl sacrificial layer. The box consisting of a broken red line shows the fabrication region of the self-supporting films. (d) Self-supporting 100-nm-thick Au thin film fabricated by NaCl sacrificial layer method.

in the silk fibroin. In Fig. 9(b), the surface geometry of the NaCl sacrificial layer was transferred to a Au thin film deposited on the Si substrate with an NaCl sacrificial layer. The surface geometry as observed in Fig. 9(b) was also found on the self-supporting Au thin film as shown in Fig. 9(c).

Figure 10 shows photographs of Au thin films of (#1) 50 and (#2) 150 nm thicknesses at each step of the process using the NaCl sacrificial layer. In the case of the Au thin film of 50 nm thickness, large wrinkles appeared when it was floating on purified water, during the releasing process as shown in (#1) of Fig. 10(b). In Fig. 10(c), it was found that both Au thin films were scooped up on perforated substrates

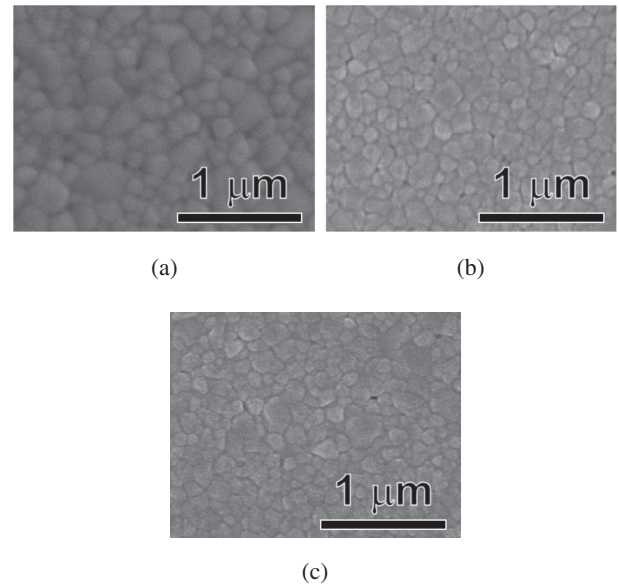


Fig. 9. SEM images of the surfaces of (a) evaporated NaCl sacrificial layer on Si substrate, (b) sputtered Au thin film on NaCl sacrificial layer, and (c) self-supporting Au thin film on perforated substrate.

but large wrinkles and cracks had appeared in the 50 nm film. Some of the self-supporting Au thin films formed from the released 50 nm film were broken as shown in (#1) of Fig. 10(c). Figure 11 shows one of the self-supporting Au thin films without the cracks formed from the 50 nm film. In Fig. 11, large wrinkles were observed on the film. In the fabrication region shown in (#1) of Fig. 10(c), there were 20 self-supporting Au thin films of 50 nm thickness and without wrinkles. In the formation from the released 150 nm film, Au thin films were all self-supporting without wrinkles in the fabrication region as shown in (#2) of Fig. 10(c).

In the self-supporting 50-nm-thick Au thin films, the cracks occurred owing to the generation of large wrinkles. The large wrinkles were generated by the effect of water waves during the releasing process because the film was too thin.

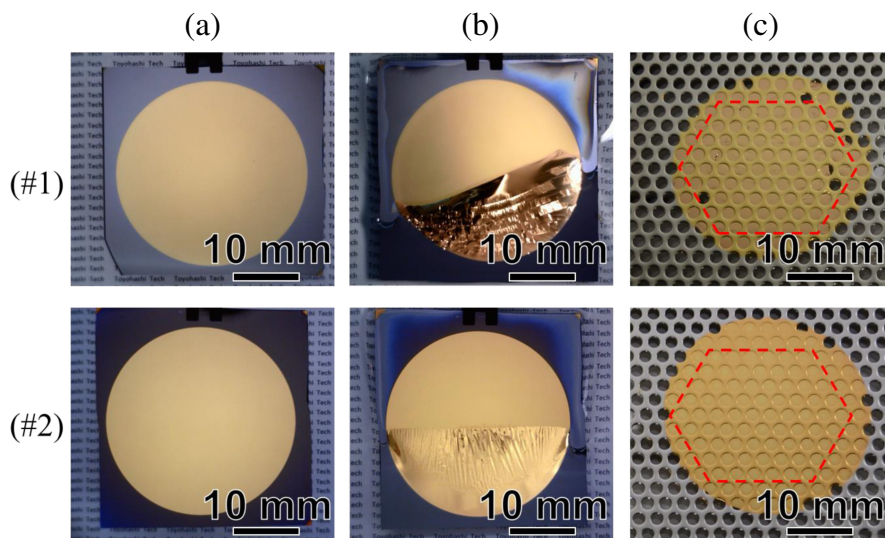


Fig. 10. (Color online) Photographs of Au thin films (a) before releasing from glass substrate, (b) on releasing from glass substrate, and (c) after scooping up on perforated substrate using NaCl sacrificial layer. The Au thin films had thicknesses of (#1) 50 and (#2) 150 nm. The boxes consisting of broken red lines show the fabrication region of the self-supporting films.

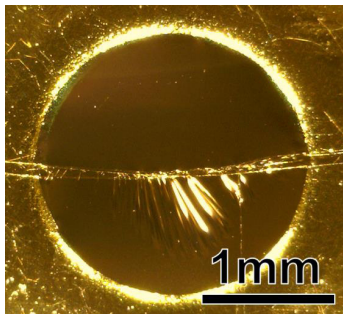


Fig. 11. (Color online) Large wrinkles on the self-supporting Au thin film of 50 nm thickness from (#1) of Fig. 10(c).

The fabricated Au thin films, which were self-supporting, 2 mm in diameter, and 50, 100, and 150 nm thick, were of high purity and can be used with the plasma sputtering method in Au deposition. The fabricated Au thin films are expected to be high-purity Au film targets for laser-driven ion acceleration experiments.

4. Conclusions

A sputtered Au thin film using a silk fibroin or NaCl as a sacrificial layer was released from a substrate. The released Au thin film was scooped up on a perforated substrate, and self-supporting Au thin films were formed on the apertures of the perforated substrate. Many small humps were found in the self-supporting Au thin films that used the silk fibroin sacrificial layer. The self-supporting Au thin film with the highest quality was obtained by using an NaCl sacrificial layer. Self-supporting Au thin films of 50, 100, and 150 nm thicknesses were fabricated.

Acknowledgments

This work was supported by JSPS KAKENHI Grant-in-Aid for Scientific Research and Toukai Foundation for Technology.

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