Shape-prediction of 3-D PTFE Microstructures Fabricated by SR ablation

M. Horade and S. Sugiyama

Abstract

Simulations for deformed shape-predictions of 3-dimensional polytetrafluoroethylene (PTFE) microstructures fabricated by Synchrotron Radiation (SR) direct etching is described in this paper. PTFE is a remarkable material, therefore the applications to various devices is expected. We aim at the application to devices which used PTFE, we research for establishment of a highly accuracy three-dimensional microfabrication technology of PTFE by using SR light. As part of their research, a simulation system for shape-prediction has been built. Since advantages of the shape-prediction system can grasp shape without experimenting, reduction of fabrication time and cost can be performed. In addition, it is a technique useful also to investigation and an elucidation of a processing mechanism. In this report, comparison with the structure fabricated by experiment and the shape computed by the shape-prediction system was performed. The simulation result was mostly in agreement with the experimental result. PTFE shows excellent material characteristic especially chemical resistance, so these researches will make to apply fabrication of \( \mu \)-TAS (Micro Total Analysis System) for Bio-medical applications. This research expects that it can profit by these designs etc.

Department of Microsystem Technology, Graduate School of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan
1. Introduction

PTFE which is a material in fluoroplastics group is remarkable as its excellent material characteristics e.g. high-voltage insulation, chemical and creep resistance, thermal stability, etc. Centering on a nonstick frying pan, a filter, etc., PTFE is used in broad fields, such as household articles, OA equipment, a semiconductor, and a car. As for PTFE, a new use is developed with these outstanding characteristics in spite of 60 years of long history every year. However, microfabrication of PTFE was difficult technology. Because due to excellent chemical resistance property, it is impossible to fabricate wet etching with chemicals (acidic, alkali) used in a lot of microfabrication like a lithography. And if PTFE heat up to high temperature, viscosity is high, therefore adaptation of molding processing is also difficult.

After that, on 1996 it was reported that technique of PTFE direct etching by using SR light [1]. It was a completely dry etching which did not use any wet etching, unlike X-ray lithography. In the using this technology, it is possible to fabricate 2.5-dimentional microstructures which has high aspect ratio of over 50. However, in order to apply the microfabrication of PTFE to Micro Electro Mechanical System (MEMS), it is preferable to be able to fabricate three-dimension microstructure with a complex form such as sloped sidewall or free-form surface.

Some research of the three-dimensional microfabrication method using synchrotron radiation has so far been done. [2] [3]. However, the all were used only with the lithography technology which used polymethylmethacrylate(PMMA), they were not used by direct etching of PTFE. Therefore, in this research, we tried to the fabrication of three-dimension PTFE microstructure by PCT (Plane-pattern to Cross-section Transfer) technique. PCT is one of methods which control the shape of structures by energy distributed to resist.

2. Fabrication and Experimental Conditions

A number of experiments were carried out using beam line number 15 (BL-15) at the superconductivity compact synchrotron radiation (SR) source "AURORA", at the SR center, Ritsumeikan University, Japan. The vacuum atmosphere at 10-5torr was provided and a substrate heater was equipped in a chamber of BL-15. Generally, in the PTFE fabrication process using SR ablation, it is noted that the etching rate becomes greater when PTFE is etched in a vacuum chamber and heated during the ablation [4]. In addition, a stage system with high flexibility is in the chamber of BL-15, and fine drive control is also possible by PC control respectively. The outline figure of BL-15 is shown in Fig.1.

The properties of SR at AURORA are, wavelength of 0.15 nm range to visible light range, applied electron energy and the maximum storage current in the experiment were 575 MeV and 300 mA, respectively. The light from AURORA penetrates two 200 µm Be
windows, and uses within the chamber the light which has a 0.15 to 0.95 nm wavelength domain.

An X-ray mask consists of a Polyimide membrane with a thickness of 50 µm and an Au absorber with a thickness of 3 µm. PTFE used the thing of 1mm thickness of Yodogawa Hu-tech Co., Ltd. A processing mechanism is shown in Fig. 2. If PTFE is exposed by SR light, PTFE will cause a photochemical reaction and main chain of PTFE is decomposed. And it changes to fluorocarbon gas and the exposed part is etched. If temperature of PTFE is high at this time, the secession rate of fluorocarbon gas can be promoted. In order to prevent polluting a mask and Be window by fluorocarbon gas, a 25 µm polyimide film was attached before each.

The Plane-pattern to Cross-section Transfer (PCT) technique was used as an exposure method controlled by giving exposure energy distribution [2]. Since PCT technique has successfully provided an arbitrary PMMA three-dimensional structure, we have recently begun to adapt PCT for exposing PTFE while the stage was moving. Fig. 3 introduces the PCT technique by a group of triangular masks. In the case of PCT when PTFE is exposed, resist is scanning. During an exposure, 2-D configuration of a mask pattern is transferring to a 3-D structure whose cross-section shape is similar to that of the mask pattern. In addition, more complex shape can be fabricated by exposing it again by rotating resist by 90 degrees after the exposure first.

3. Processing Depth Simulation
3.1 Derivation of Etching Rate

First of all, in order to derive etching rate, a relation between beam current and a processing depth was investigated. PTFE was exposed by SR light. When exposure time is 30
minutes, and the PTFE surface temperature is changed with 110°C, 140°C, 170°C, and 200°C, respectively, the processing depth was checked. Fig. 4 shows the relation between a beam current and a processing depth.

If an approximate expression is formulated by based on this data and it divided by exposure time, the etching rate per unit time to beam current is derivate. However, beam current decreases little by little as time passes. For example, the case that PTFE surface temperature is 170°C is explained. Table 1 shows the beam current at the time of an exposure start, the beam current at the time of an end, and the processing depth. That is, the processing depth will not be obtained compared with the case where it is assumed that a beam current is constant and does not decrease. As shown in Fig. 5, an actual etching rate (solid line) becomes a somewhat larger value than the value divided by 30 (dashed line) which is exposure time.

Table 1 Beam Current and Processing Depth

<table>
<thead>
<tr>
<th>Beam Current (mA)</th>
<th>Finish Current (mA)</th>
<th>Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250.0 mA</td>
<td>232.2 mA</td>
<td>68.544 µm</td>
</tr>
<tr>
<td>210.0 mA</td>
<td>194.2 mA</td>
<td>40.245 µm</td>
</tr>
<tr>
<td>170.0 mA</td>
<td>160.8 mA</td>
<td>29.180 µm</td>
</tr>
</tbody>
</table>

Fig. 3 PCT technique exposure

Fig. 4 Beam Current VS Processing Depth

Fig. 5 Derivation of Etching rate (170°C)
It is difficult to check the etching rate to change of this beam current in real time. Therefore, as shown in Fig. 6, the etching rate in the state where it increased to some extent will be used. In order to obtain a reliable etching rate, we have to decide this increase of stock moderately. Then, validity of the etching rate in consideration of this expected increment is evaluated. The processing depth in arbitrary time is computed from this etching rate, and comparison with an experimental value is performed. When there are many errors with an experimental value, an increase of stock is adjusted again and validity is evaluated. If it carries out by repeating this work and the data near an experimental value is obtained, this etching rate is used for processing depth or three-dimensional shape-prediction simulation.

3.2 Evaluation of Validity

As shown in Fig.6, relation of between time and a beam current reduction is set to (A). And relation between beam current and an etching rate is set to (B).

\[ y = f(t) \] (A)
\[ y = g(\text{current}) \] (B)

The processing depth in the arbitrary exposure time \((t=\text{Time})\) can be expressed with (C).

\[ y = \int_{0}^{\text{Time}} g(f(t)) \, dt \] (C)

The processing depth in exposure time 30 minutes can be expressed with (D).

\[ y = \int_{0}^{30} g(f(t)) \, dt \] (D)

Using the method introduced for foregoing section, the derivate etching rate at the case that PTFE surface temperature is 200°C is shown in Fig. 7 (A). And using this etching rate, the relation of the current beam and the processing depth at the case of exposure time 30 minutes are shown in Fig. 7 (B). Moreover, experimental results are also shown. The figure shows that the experimental value and the simulation result are mostly in agreement. Therefore, it is judged that the reliability of this etching rate is very high. When temperature is 140°C, it is similarly shown in Figs.8. This figure also shows that the experimental value and the simulation result are mostly in agreement. Therefore, it is judged that the reliability of these etching rates is very high.
4. Shape-Prediction for 3-D Microstructures

Since the PCT technique is the method of scanning resist to the mask, it can give exposure distribution to PTFE. Therefore, in a part with PTFE, only when a membrane part of the mask overlaps with the PTFE upper surface, etching is performed. If absorber width is set to $X$ (µm), exposure time is set to Time ($t=Time$) and scanning width is set to scan (µm) as shown in Fig. 9, the processing depth ($Depth(x,y)$) in the arbitrary parts ($(x,y)$) on PTFE will be set to (E).

$$Depth(x, y) = \int_0^{Time} g(f(t)) \cdot \frac{scan}{1500} \cdot \frac{dt}{1500} \cdot \frac{1500 - X}{1500} \quad \text{(E)}$$

![Fig.9 Depth Simulation of Using PCT Technique](image)

The processing depth at a case of making it rotate 90 degrees and exposing again after the 1st exposure, should just add the processing depth by the conditions before rotation and
the conditions after rotation. The depth determined by the conditions before rotation is set to \( \text{Depth}_{\text{before}}(x, y) \) and after rotation is \( \text{Depth}_{\text{after}}(x, y) \), the processing depth (\( \text{Depth}'(x, y) \)) in the arbitrary parts \((x,y)\) will be set to (F)

\[
\text{Depth}'(x, y) = \text{Depth}_{\text{before}}(x, y) + \text{Depth}_{\text{after}}(x, y)(F)
\]

### 4.1 Results of Triangular Mask

Result at the case of using a triangular mask as shown in Fig. 10 (A) is shown. SEM photograph of the structure at the case that PTFE surface temperature is 140°C is shown in Fig. 10 (B), and shape-prediction result is shown in Fig.10(C). SEM photograph of the structure and shape-prediction result at the case that PTFE surface temperature is 200°C is shown in Fig. 10 (D). SEM photograph of the structure and shape-prediction result when exposure by rotating 90 degrees after 1\text{st} exposure is shown in Fig. 10 (E).

![Fig.10 Results of Using Triangular Mask](image)

### 4.2 Results of Semicircular Mask

Result at a case of using a semicircular mask as shown in Fig. 11 (A) is shown. SEM photograph of the structure and shape-prediction result at the case that PTFE surface temperature is 200°C is shown in Fig. 11 (B). SEM photograph of the structure and shape-prediction result when exposure by rotating 90 degrees after 1\text{st} exposure is shown in Fig. 11 (C).

### 4.3 Results of Sine-curved Mask

Result at the case of using a sine-curved mask as shown in Fig. 12 (A) is shown. SEM photograph of the structure and shape-prediction result at the case that PTFE surface
temperature is 200°C is shown in Fig. 12 (B). SEM photograph of the structure and shape-prediction result when exposure by rotating 90 degrees after 1st exposure is shown in Fig. 12 (C).

![Fig.11 Results of Using Semicircular Mask](image1)

![Fig.12 Results of Using Sine-curved Mask](image2)

5. Conclusion

It succeeded in fabrication of three-dimensional structures of PTFE. Construction of the simulation system for shape-prediction was aimed at this time. The algorithm which can reconstruct a processing mechanism was devised and the reliability of various parameters was also examined. Comparison with the simulation result is computed using this system and an experimental result was performed. The simulation result was mostly in agreement with the experimental result. PTFE shows excellent material characteristic especially chemical resistance, so these researches will make to apply fabrication of µ-TAS for Bio-medical applications. This research expects that it can profit by these designs etc.

References