Nano-fabrication and Functionalization of Crosslinked PTFE Using Focused Ion Beam

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It was demonstrated that the nano/microfabrication and functionalization for crosslinked Polytetrafluoroethylene (RX-PTFE) were carried out using focused ion beam (FIB). The fine pattern of the regularly nano-scale square array holes with 300 nm square size were fabricated by FIB direct etching. The fabricated samples were functionalized by post grafting reaction using trapped free radicals induced by FIB irradiation, and the samples were successively sulfonated. The obtained samples were treated by the mixture solution of KOH/KCl to make potassium form, and observed by FE-SEM with EDX spectroscopy. The signals correspond to potassium atom were detected at the holes in fabricated area of RX-PTFE. On the other hand, the signals of potassium formed sulfonic group were hardly detected at the distance of 10 μm from the hole’s center in the fabricated area.

Keywords: FIB, crosslinked PTFE, nano-fabrication, grafting functionalization, EDX spectroscopy

1. Introduction
PTFE has excellent properties such as chemical stability, thermal stability and so on. So, PTFE has been used in various industrial fields. Recently, it was confirmed that PTFE was crosslinked by EB or γ-rays irradiation at selective conditions [1-4]. Crosslinked PTFE (RX-PTFE) shows the improvement in radiation resistance and wear resistance properties, compared with PTFE. In our recent studies, microfabrication of PTFE has been carried out using synchrotron radiation [5-8], or FIB [9, 10]. According to ion beams irradiation effect on fluorinated polymers, the trapped free radicals were produced in polymer matrix [11].

In this study, it was attempted to fabricate nano/microstructure using focused ion beam (FIB), and to functionalize the structure with the induced trapped free radicals in RX-PTFE matrix by FIB.

2. Experimental procedure
The scheme of nano/microfabrication and functionalization for RX-PTFE is shown in Fig. 1. The process consists of 3 steps, which are (1) preparation of materials, (2) nano/microfabrication using FIB, and (3) functionalization by radiation-grafting and sulfonation.

2.1 Preparation of materials
PTFE dispersion (FLUON® XAD911, average φ0.25 μm, 60 wt%, ASAHI GLASS Fluoropolymers Co., LTD.) was used for the experiments. About 100 μl PTFE dispersion was coated by spin-coater (SPINCOATER 1H-DX2, MIKASA CO., LTD.) on 2 cm × 2 cm square silicon wafers (cut from 4 inch size, Shin-Etsu Chemical Co., LTD.). After the process, the samples were sintered at 360 °C for 30 min in
nitrogen atmosphere. RX-PTFE were obtained by electron beam irradiation (installed at RISE, Waseda Univ., Curetron®. NHV Corp., accelerating voltage: 200 kV, beam current: 1 mA) with a dose of 600 kGy at 335 ± 5 °C under N₂ gas atmosphere.

2.2 Nano / micro fabrication
The nano / micro fabrication was performed using FIB (SMI2050 Seiko Instruments Inc., installed at ISIR, Osaka University, ion source: Ga⁺, accelerated voltage: 30 kV). The samples were placed perpendicularly to FIB in a vacuum chamber and irradiated by FIB. FIB was scanned to etch desired patterns by a computer controlled scanning system. Irradiation parameters of FIB are listed in Table 1. Fig. 2 shows the fabrication pattern map used for the functionalization experiments.

2.3 Functionalization of nano / microfabricated material
After fabrication using drawing pattern as shown in Fig. 2, the trapped free radicals in RX-PTFE were converting to peroxy radicals by exposing in air. The samples were grafted with styrene monomer by immersing in purified styrene monomer (Wako Pure Chemical Industries Ltd.) at 80 °C for 1.5 h under vacuum [12, 13]. And then, the samples were washed with cyclohexane and carbon tetrachloride for 2 days and dried [12, 13].

Then the grafted samples were sulfonated with the mixture solution of chlorosulfonic acid and carbontetrachloride (1.99 vol.%) at room temperature for 24 h [12].

<table>
<thead>
<tr>
<th>Table 1. Irradiation parameters of FIB</th>
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<tbody>
<tr>
<td>Beam spot size (FWHM) Φ [nm]</td>
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<tr>
<td>23</td>
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</table>

Figure 2. Fabrication pattern map used for the functionalization experiments. (hole: 1.6 μm × 1.6 μm square, hole’s distances: 6.0 μm, makers for SEM observation: 25 μm × 25 μm square)

2.4 Measurements
The obtained functionalized samples were soaked into 0.1M KOH with 0.5M KCl solution for 24 h to make potassium form. And then, these were also purified with deionized water.

The obtained samples were measured by field emission scanning electron microscope (FE-SEM, S-4500S HITACHI Corp.), and Energy Dispersive X-ray Spectroscopy (EDX, QuantumDry, kevex) to evaluate an atom ratio measurement of the obtained sample.

3 Results & Discussion
Fig. 3 shows FE-SEM image of nano-filter pattern of RX-PTFE. The hole of obtained filter was 300 nm square size.

Figure 3. FE-SEM image of nano-filter pattern of RX-PTFE (beam current: 9 pA, fluence: 5.0 × 10¹⁵ ions/cm², beam spot size (FWHM) Φ 13 nm, hole: 300 nm square size).
It was confirmed that the fine pattern of the regularly nano-scale square array holes in RX-PTFE was fabricated by FIB direct etching.

Fig. 4 shows FE-SEM images of the functionalized sample after FIB fabrication with the template as shown in Fig. 2. After the fabricated RX-PTFE was separated from Si wafer, RX-PTFE surface was observed at opposite side of the surface of FIB irradiation by FE-SEM, as shown in Fig. 4. It was thought that the grafting yields at the opposite side would be lower than that at irradiated side. From SRIM-2008 code [14], it would be considered that the trapped radicals in the opposite side produced by FIB irradiation were lower, compared with irradiated side.

It was observed that most of the holes fabricated by FIB direct etching were closed by styrene-grafting, as shown in Fig. 4 (c). A part of the holes’ shape was distorted, as shown in Fig. 4 (b). According to our previous studies on FIB direct etching for fluorinated polymers, the fabricated condition in the experiments should be penetrating the sample’s thickness [9].

![Figure 4. FE-SEM image of fabricated area. (a): overall view of fabrication area. (b): magnitude distorted fabricated hole. (c): magnitude buried fabricated hole. (Tilt: 20°)](image)

Fig. 5 shows EDX spectra of functionalized area at the center of fabricated hole as shown in Fig. 4 (b) and reference point at 10 µm from the center. The several peaks were observed as summarized in Table 2 [15]. The peak at 0.282 keV, and the weak peaks at 0.523 keV and 0.677 keV which correspond to C, O, and F atoms were attributed to RX-PTFE, respectively. The signals at 1.740 keV, 1.739 keV and 1.832 keV of Kα1, Kα2, and Kβ1 from Si atom were observed, respectively, and were attributed to substrate (Si wafer). Moreover, the peaks at 2.838 keV, 2.833 keV, 2.050 keV and 2.046 keV of Lα1, Lα2, Mα1, and Mα2 from Pt and Pd atoms were detected, respectively, and were attributed to electric coating layer avoiding electron charge up effect during SEM observation.

![Figure 5. EDX spectra at the center of fabricated hole and the reference point.](image)

### Table 2. Characteristic X-ray energy

<table>
<thead>
<tr>
<th>Characteristic X-ray</th>
<th>Energy [keV]</th>
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<tbody>
<tr>
<td>Kα carbon (C)</td>
<td>0.277</td>
</tr>
<tr>
<td>Kα oxygen (O)</td>
<td>0.525</td>
</tr>
<tr>
<td>Kα fluorine (F)</td>
<td>0.677</td>
</tr>
<tr>
<td>Kα1 silicon (Si)</td>
<td>1.740</td>
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<tr>
<td>Kα2 silicon (Si)</td>
<td>1.739</td>
</tr>
<tr>
<td>Kβ silicon (Si)</td>
<td>1.832</td>
</tr>
<tr>
<td>Kα1 sulfur (S)</td>
<td>2.307</td>
</tr>
<tr>
<td>Kα2 sulfur (S)</td>
<td>2.306</td>
</tr>
<tr>
<td>Kβ1 sulfur (S)</td>
<td>2.464</td>
</tr>
<tr>
<td>Kα1 chlorine (Cl)</td>
<td>2.622</td>
</tr>
<tr>
<td>Kα2 chlorine (Cl)</td>
<td>2.620</td>
</tr>
<tr>
<td>Kα potassium (K)</td>
<td>3.313</td>
</tr>
<tr>
<td>Kα2 potassium (K)</td>
<td>3.310</td>
</tr>
<tr>
<td>Kβ potassium (K)</td>
<td>3.589</td>
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<tr>
<td>Lα1 palladium (Pd)</td>
<td>2.838</td>
</tr>
<tr>
<td>Lα2 palladium (Pd)</td>
<td>2.833</td>
</tr>
<tr>
<td>Mα1 platinum (Pt)</td>
<td>2.050</td>
</tr>
<tr>
<td>Mα2 platinum (Pt)</td>
<td>2.046</td>
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</table>
The peaks at 2.307 keV, 2.306 keV, 2.464 keV from S atom were observed, respectively, and were attributed to sulfonic group in grafted side chain. Moreover, the observed signals at 2.622 keV, 2.620 keV of Kα1, Kα2 were attributed to Cl atom, respectively. The observed signals at 3.313 keV, 3.310 keV and 3.589 keV of Kα1, Kα2, and Kβ were attributed to K atom, respectively. Both observed atoms of K and Cl, could be due to the re-crystallized potassium chloride (KCl crystals) and the K-formed sulfonic group in the functionalized sample.

![Graph](image)

Figure 6. Relationship between distance from the center point of fabricated hole and the atom ratio of K/Cl.

The signal intensities of observed peaks of K atom and Cl atom at the fabricated holes were higher than those at the reference point. The atom ratio of K/Cl at the fabricated hole calculated from Fig. 5 was 1.48. In the case of atom ratio at the reference point, the ratio showed 0.98. The ratio at the fabricated hole was higher than that at the reference point. This would be indicating that the trapped free radicals were induced by FIB irradiation at the fabricated hole, and then the grafting reaction occurred at this point.

Fig. 6 shows relationship between distance from the center point of fabricated hole and the atom ratio of K/Cl calculated by EDX spectra. The measuring point was related for 11 points by 1 μm step from the center point.

As shown in Fig. 6, it was found that the ratio at 2 μm distance from the center point showed a maximum value. And then, the ratio would tend to decrease with increasing of distance from the center. These results are indicating that the point at around 2 μm from the center point was functionalized area due to grafting reaction, because the fabricated hole’s size was about 1.4 μm square as shown in Fig. 4.

That is, there was K-formed sulfonic group in the fabricated hole. On the other hand, K-formed sulfonic group was hardly observed in the out of functionalized area, and KCl crystals at the surface of the sample would be only detected by EDX spectra.

**4. Conclusion**

It was attempted that the nano / microfabrication for RX-PTFE and functionalization were carried out using FIB. The fine pattern of the regularly nano-scale square array holes with 300 nm square size, was fabricated.

The fabricated samples were functionalized by post grafting reaction. The obtained functionalized sample was treated by the mixture solution of KOH/KCl solution to make potassium form, and observed by FE-SEM with EDX spectroscopy. It was observed that most of the holes fabricated by FIB were functionalized by K-formed sulfonic group. On the other hand, K-formed sulfonic group was hardly presence in the out of fabricated area.

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**References**


