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Fabrication of Nanosized Structures on Nafion Membranes by Thermal Nanoimprinting

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SUMMARY We demonstrated a novel technique to fabricate nanosized structures on a Nafion membrane, using thermal nanoimprinting with a $5 \times 5\,\mu\text{m}^2$ square pattern Si mold without any polymer damage. A 24 MPa thermal imprinting pressure was used for 10 min. We observed high aspect ratio (~1:10) pillars on the surface after imprinting at 200°C. Finally, we used a novel quartz mold with a 200 nm resolution dot pattern.

key words: *Nanoimprinting, Ion-conductive polymer, Nafion, Flexible devices*

1. Introduction

Ion-conductive polymers are key materials used in various flexible devices such as gas-sensors, fuel cells, and micro-electromechanical systems (MEMS) [1]–[4]. In particular, Nafion (DuPont), comprised of a polytetrafluoroethylene (PTFE) backbone and sulfonated tetrafluoroethylene side chains, is a widely used ion-conductive polymer material [3]–[5]. We recently demonstrated a novel electrode fabrication process on a Nafion surface using a plasma surface modification technique [6]. In our previous reports, we showed that nanosized structures on the Nafion surface improved its electronic properties and the adhesion shear strength of the metal-Nafion interface [7]. This plasma treatment process effectively increased the ion transport surface area, providing a fabrication method of a metal-Nafion surface applicable for use in fuel cells, MEMS, or flexible devices. However, this plasma treatment has some serious problems due to it being a high energy process. The Nafion polymer chains are broken down by the high energy plasma during the plasma treatment. The surface nanostructures are then formed by a re-polymerization reaction. During plasma treatment, numerous ion-conductive side chains on the surface are damaged and destroyed. A number of nanofabrication methods that use plasma have a significant problem of Nafion membrane damage [8]–[10]. Therefore, it is crucial to develop a damage-free nanostructure fabrication method on ion-conductive polymers. The purpose of this study was to adapt a nanoimprinting method for ion-conductive polymer materials, as these can form metal electrodes suitable for flexible device applications.

Nanoimprinting is an excellent potential nanostructure fabrication method for ion-conductive polymers due to it being an inert fabrication technique compared to plasma processes, electron-beam lithography, and other nano-fabrication processes. With a micrometer resolution, imprinting techniques have been applied to fuel cell and MEMS applications [11]–[14]. However, these imprinted features have a low aspect ratio (~1:1) and provided minimal information about the nanoimprinting conditions. In addition, there is limited data available related to the nanoimprinting applicability on Nafion with a resolution below 200 nm.

Here, we demonstrate the fabrication of nanosized structures on a Nafion membrane using a thermal nanoimprinting method. To optimize the thermal nanoimprinting conditions, we investigated various thermal nanoimprinting conditions for fabrication of nanostructures on the Nafion membrane surfaces, including examination of the surface morphologies relative to imprinting conditions. In addition, the fabrication technique of our novel quartz mold, using self-assembled nanoparticles, is described. In our previous report [15], size controllable, self-assembled tungsten oxide (WO_3) nanoparticles were synthesized on a quartz surface by the metal-organic decomposition (MOD) method. The average diameters of these synthesized WO_3 nanoparticles are easily scaled from 75 nm to 200 nm by changing the baking temperature. In this study, we used these size controllable WO_3 nanoparticles in place of a traditional lithographic method, as it is difficult to tch masks for fabricating nanoimprinting molds. This novel method enables the fabrication of a nanoimprinting mold with a sub-100 nm resolution without using expensive instruments such as electron beam (EB) lithography, focused ion beam (FIB) patterning, or liquid immersion photolithography.

2. Experimental

Nafion 117 membranes were obtained from Sigma-Aldrich. Si molds with a $5 \times 5\ \mu$m square pattern were used for this experiment (Fig. 1(a)). The unique quartz mold with a 200 nm resolution pattern was fabricated by first synthesizing the WO_3 nanoparticles on a quartz surface using the MOD at a 900°C baking temperature [15]. In this paper, the average diameter of the synthesized WO_3 nanoparticles was 200 nm. A reactive ion etching (RIE) of this nanoparticle-coated substrate was performed using a parallel-plate type

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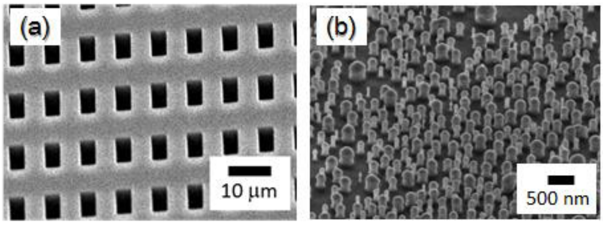

Fig. 1 Surface morphology SEM images of (a) the Si mold with a 5×5 μm square pattern and (b) our novel 200 nm resolution mold used in this study.

radio frequency plasma system at 13.56 MHz. The plasma power density was 1.35 W/cm^2, and a mixture of CF_4 and O_2 gases was used for the quartz vertical etching. The mixture ratio of the CF_4:O_2 was 54:17 at a 5 Pa gas pressure and an approximate 30 nm/min etching rate. The etching depth was adjusted to 300 nm, finally giving an original quartz mold with a 200 nm resolution, as shown in Fig. 1(b).

This handmade 200 nm resolution thermal nanoimprinting mold was used in this experiment. The maximum imprint pressure and temperature of our nanoimprinting device were 50 MPa and 300°C, respectively. In this experiment, the imprint pressure and time used were 24 MPa and 10 min, respectively. The imprint temperatures were varied from room temperature up to 200°C to find the optimal temperature. The surface morphologies of the molds and imprinted Nafion surfaces were then observed using a scanning electron microscope (SEM).

3. Results and Discussion

For all of the varied nanoimprinting conditions in our experiment, the mold release behavior (i.e., the demolding process) was very smooth. The Nafion membranes easily released from both the Si and quartz molds. This release behavior likely results from the fluorinated surface consisting of the Nafion's polytetrafluoroethylene (PTFE) backbone. This release behavior seen for the Nafion surface nanoimprinting process is one of its numerous advantages.

Figure 2(a)–(d) show the SEM images of the nanoimprinted Nafion surfaces treated at room temperature (R.T.) (Fig. 2(a)), 110°C (Fig. 2(b)), 140°C (Fig. 2(c)), and 170°C (Fig. 2(d)) using the Si mold with the 5×5 μm square pattern.

The height of the Nafion sample nanoimprinted pillars at R.T. was below 1 μm (Fig. 2(a)). With increasing temperature during the nanoimprinting process, the height of the square pillars also increased (Fig. 2(b)–(d)). In particular, the height of the 170°C sample increased significantly to an approximate 20 μm. The reported glass transition temperature of Nafion membranes range between 120–140°C [16]. As these pillars grow from the Nafion surface during nanoimprinting, they become smoother due to the polymer's increased fluidity; this is because the temperature is rising above its glass transition temperature. According to these results, a temperature of at least 140°C is required to successfully nanoimprint the Nafion.

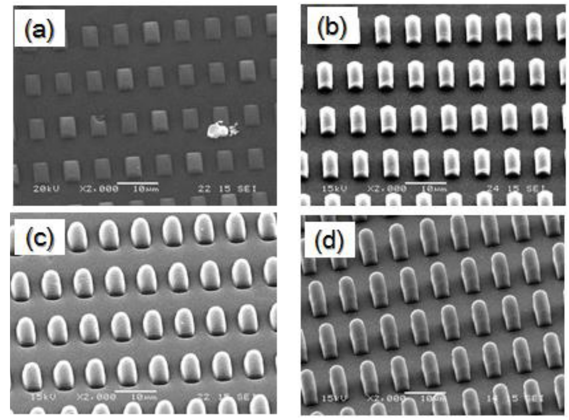

Fig. 2 Surface morphology SEM images of the thermally nanoimprinted Nafion films under 24 MPa at (a) R.T., (b) 110°C, (c) 140°C, and (d) 170°C.

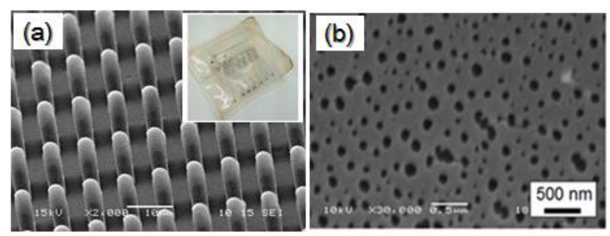

Fig. 3 (a) SEM image of the imprinted Nafion under 24 MPa at 200°C using the Si mold and (inset) its optical photograph. (b) SEM image of the imprinted Nafion surface at 170°C using the novel quartz mold.

Figure 3(a) shows the SEM image of a Nafion surface imprinted at 200°C using the Si mold. The height of these imprinted nanopillar features is higher than 40 μm. These high aspect features are valuable for various flexible device applications including gas sensors, fuel cells, and MEMS devices. However, as shown in the inset of Fig. 3(a), the Nafion membrane appears scorched, with a light brown color observed after the nanoimprinting process. We concluded that this change in its outward appearance was the result of oxidation and the glass transition derived from the sulfonic acid side chain around 195°C [16]. A similar change in appearance was observed for damaged Nafion membranes after long plasma treatments [6]. Therefore, we suggest that the maximum temperature for Nafion nanoimprinting should be limited to approximately 195°C. Finally, we demonstrated the applicability of the 200 nm resolution mold for Nafion nanoimprinting. Figure 3 (b) shows the nanoimprinted Nafion surface using our original mold at 170°C. The minimum diameter of the imprinted holes is approximately 50 nm. This preliminary result of a small feature resolution indicates that the thermal nanoimprinting method is effective and advantageous for fabrication of nanosized structures on a Nafion surface.

4. Summary

We demonstrated a nanosized-structure fabrication technique on a Nafion membrane utilizing the nanoimprinting method. High aspect ratio pillars were observed on the

Nafion's surface after imprinting at 200°C; however, damage of the polymer surface was observed. Finally, we used a novel quartz mold with a 200 nm resolution nanodot pattern to imprint the Nafion membrane. The minimum resolution is approximately 50 nm according to the imprinted pattern of the original mold.

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