Fabrication of Self-standing Polystyrene Thin Films with Fine Through Holes by use of Water Soluble Resin Sacrificial Layer

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A simple fabrication process is developed for self-standing resin films with well-defined through-holes by use of imprint technology. Polyvinyl alcohol film, which can be dissolved in water, is used as a sacrificial film. A commercial bi-layer film sheet, where polyvinyl alcohol (PVA) film is laminated on polyethylene terephthalate (PET) film, is used. A mold pattern is directly transferred to the PVA film in the bi-layer film sheet, and polystyrene (PS) resin is coated on the patterned PVA film. The PVA sacrificial film is removed in water. A defect free PS self-standing film of 0.7 μm in thickness can be obtained in the fixing frame with 5 mm diameter hollow. Through-holes of 2.5 μm square are successfully fabricated in the PS self-standing film.

Keywords: Polyvinyl alcohol film, Casting, Polystyrene, Self-standing, Through hole

1. Introduction
Self-standing membranes with well-defined through-holes have wide applications such as microfiltration [1], gas exchange [2], stencil masks [3-5]. Self-standing membranes with well-defined through-holes have been fabricated by use of micro fabrication process based on silicon technology [6-10]. Membrane with very high aspect through-holes was also fabricated by anodic porous alumina [11]. Although many processes have been proposed, these processes are usually complicated.

Nano imprint lithography (NIL) is one of the most important techniques for nano pattern fabrication. Both micro- and nano-patterns have been fabricated with high resolution, high throughput, and low cost [12,13]. Self-standing membranes with well-defined through-holes have been fabricated by imprint process [14,15]. However, it is considered that the imprint process has serious problems for fabricating self-standing resin films with through-holes as described below. Figure 1 shows a typical fabrication process by conventional imprint process. The process can be divided into two major steps. One is imprint step (Figs. 1(a) and (b), which are press and demolding, respectively) and the other is transfer step, where the film is transferred from substrate to fixing frame with hollow (Fig. 1(c)). In the imprint step, a moderate sticking force between the substrate and the resin film is required for the successful demolding. However, the sticking force

![Fig. 1. Basic process flow of self-standing resin film fabrication by imprint technology.](image-url)
should be as small as possible in the transfer step, because the fragile thin film must be broken by small sticking force between the substrate and the resin film as shown in Fig. 1(d). The film transfer is one of the most critical issues for fabricating self-standing film by imprint process. It is considered that the patterned resin film should be supported by a sacrificial film as shown in Fig. 2. The sacrificial film must have enough strength in order to avoid the film break during the transfer step. Moreover, the sacrificial film should be easily removed after the transfer. The sacrificial film must be selected carefully for satisfying these conditions.

In this paper, simple process is developed for fabricating self-standing thin films. A water soluble resin is used as the sacrificial film in the transfer process. The patterned films are fabricated by use of two processes, one is the conventional thermal imprint process and the other is the casting process. A 0.7 μm thick self-standing polystyrene film with 2.5 μm through-holes is successfully fabricated in the fixing film with 5 mm diameter hollow.

2. Transfer process by use of water soluble resin
The following three properties are required for the sacrificial film, (1) easy remove without damage of patterned resin film, (2) enough strength for the transfer step, and (3) easy release from the substrate.

In the developed process, a commercial polyvinyl alcohol (PVA) film laminated on polyethylene terephthalate (PET) film (SO sheet supplied by Aicello [16]) is used. The thicknesses of PVA and PET films are 30 μm and 75 μm, respectively. This bilayer film is named as PVA/PET sheet in this paper. The PVA film is used as the sacrificial film. Since PVA is water soluble resin, this film can be easily removed in water without film damage for various resins. By use of this unique property, PVA is often used as the sacrificial film [17-20]. For PVA/PET sheet, the PVA film has enough thickness, and the film can work as supporting film for the thin patterned resin. The PVA film is soft and difficult to handle during the process, but the PVA/PET sheet has enough strength for easy handling. Since the PET film is hard and strong, it can be used as the substrate in Fig. 1. Then, the sample preparation becomes very simple and low cost, because no substrate such as Si wafer and no PVA coating step are necessary. Moreover, the PET film can be easily removed by hand. According to the superior properties of PVA/PET sheet, this sheet must be suitable for the sacrificial process [21] to fabricate self-standing thin resin films.

3. Imprint process
Small holes are fabricated into thin resin film by a conventional thermal imprint. The fabrication process is shown in Fig. 3. Polystyrene (PS) film is used as the resin film, because PS is one of the most popular resin and low cost. PS film of 0.7 μm thickness is coated on the PVA film of PVA/PET sheet. The PS film is pressed by Si mold (Fig. 3(a)). The press pressure and temperature are 10 MPa and 150 °C, respectively. The press time is 10 min. After the demolding, the PVA/PET sheet with patterned PS film is stuck to fixing frame with 5 mm diameter hollow, and the PET film of PVA/PET sheet is peeled off by hand (Fig. 3(b)). The patterned PS film...
supported by the PVA film is put into hot water of 70 °C for 30 min (Fig. 3(c)). After drying in hot oven of 80 °C, thin self-standing PS film is obtained (Fig. 3(d)). The self-standing PS film can be obtained in 5 mm diameter hollow. The film damage can be hardly seen by eye observation. Figure 4(a) shows the used Si mold. The mold has square pillar patterns of 5 × 5 μm. The pillar height is about 5 μm. The SEM picture of fabricated self-standing PS film is shown in Fig. 4(b). It is clear that a large part of hole patterns are covered. Although the pillar height of the mold pattern is about 8 times as large as the PS film thickness, the percentage of complete penetration holes is less than 10%. At the high temperature of 150 °C, the thick sacrificial PVA film also becomes soft. Then, the PS film is pushed downward by the pillar pattern, and must be largely extended to vertical direction as shown in Fig. 5. For the conventional nano-imprint process, residual layer in the pattern bottom is usually removed by O₂ contained plasma [22]. In the same way, the bottom PS layer in the hole pattern can be removed by O₂ contained plasma treatment after the demolding and complete penetrate PS holes may be obtained. However, the additional process is required and the PS film thickness decreases by O₂ contained plasma treatment. The decrease of the film thickness directly induces the loss of film strength. Then, it is afraid that O₂ contained plasma treatment may induce fatal error for fabricating self-standing film.

4. Casting process

It is difficult to obtain complete penetrate holes in the self-standing PS film by the imprint process. Then, we try to fabricate self-standing PS film with small through holes by casting process [23]. The process flow is shown in Fig. 6. First, pillar pattern is fabricated in the PVA film of PVA/PET sheet by
thermal imprint process (Fig. 6(a)). The press pressure and temperature are 10 MPa and 150 °C, respectively. The press time is 20 min. Next, PS resin is coated on the PVA pattern. The PVA/PET sheet with patterned PS film is stuck to the fixing frame and the PET film of PVA/PET sheet is peeled off by hand (Fig. 6(b)). After the preparation of the sample on the fixing frame, the following processes are completely the same as the imprint process (Figs. 6(c) and 6(d)). No PS extend to the vertical direction induces in the casting process. The fabricated PVA pattern is shown in Fig. 7(a). The square pillars of about 2.5 μm can be successfully obtained. The pillar height is about 2.5 μm. Figure 7(b) shows the pillars after the PS coating. It is found that PVA top is appeared after PS coating. The PS thickness is estimated about 0.7 μm by comparing the PVA pillar heights of Fig. 7(a) and Fig. 7(b). Figure 8 shows a visual view of the fabricated self-standing PS film.

It is found that defect free self-standing film can be obtained in the 5 mm diameter hollow of the fixing frame. Figure 9 shows the SEM pictures of the fabricated self-standing PS film. From Fig. 9(a), it is confirmed that over 90% holes are completely through the PS film, although a few holes are

Fig. 7. SEM pictures of (a) fabricated PVA mold and (b) PVA mold after PS coating for casting process.

Fig. 8. Visual observation of fabricated self-standing PS film by casting process.

Fig. 9. SEM pictures of fabricated self-standing PS film by casting process, (a) low magnification picture for wide area observation and (b) high magnification picture for detail observation of hole pattern.
covered by thin PS layer as shown by arrows. From Fig. 9(b), it is found that the size of the square through-holes is 2.5 μm, which is same as the PVA pillar size.

5. Conclusion
A process for fabricating self-standing resin films with small through-holes is developed. Polystyrene (PS) is used as the thin resin, because PS is one of the most popular resins and low cost. A commercial PVA/PET bilayer film is used in the process. The PVA film of PVA/PET sheet is used as the sacrificial film for thin PS film transfer and the PET film is used as the substrate. For the casting process, the fabrication process consists of thermal imprint of PVA film and PS resin casting. The process is simple because no lithography and plasma processes are used. The self-standing PS film with through-holes of 2.5 μm square can be successfully fabricated. The self-standing PS film is obtained in the fixing frame with 5 mm diameter hollow without film defect.

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