Preparation of Self-Organized Porous Polymer Masks for Si Dry Etching

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Summary: Self-organized honeycomb-patterned polymer films were prepared by using condensed water droplet arrays as templates. Porous polymer masks for dry etching were easily prepared on Si substrates by peeling off the honeycomb-patterned films. After dry etching, hexagonally-arranged micro-pores were formed on the surface of Si substrates.

Keywords: porous polymer mask; self-organization; silicon dry etching

Introduction

Dry etching is an important process of Si technology[1]. Therefore, dry etching masks prepared by simple, inexpensive, and low energy consumption processes are strongly required. Block copolymer lithography is one of the emerging methods of Si patterning technology. Microphase separation structures of periodic nano-scale patterns formed in block copolymer thin film act as dry etching masks[2,3]. Another example is ‘‘colloidal lithography’’, which uses single layer of colloidal crystal as dry etching masks[4–7]. By using self-assembly techniques, dry etching masks having periodic nano-structures can be easily prepared.

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We have previously reported the simple preparation methods of polymer nano and micro patterns, such as honeycomb-patterned porous structures, regularly arranged dot-pattern, line and space pattern, ladder-patterned structures and so on, by using self-organization techniques[8]. Honeycomb-patterned porous polymer films can be prepared by casting polymer solutions onto solid substrates under humid conditions[9–13]. During evaporation of solvents, water droplets condense onto the surface of polymer solution, and then, porous polymer films can be formed by using these water droplets as templates. Subsequently, polymer pincushion films with hexagonally arranged spike-structures were prepared by simply peeling off the top layer of the honeycomb-patterned films[14,15]. These spike-structures remained on bottom layer can provide various hydrophobic surfaces as well as honeycomb-patterned polymer films[16–20]. By chenging the preparation conditions including casting volume or solution concentration, the penetration of bottom layer of the film can be controlled.

Here we focus on the top layer of the honeycomb-patterned film after peeling from bottom layer because the top layer has uniformly arranged penetrated pores regardless of the preparation conditions, which can be applicable to dry etching mask. In this report, we describe a simple and easy preparation method of the dry etching mask from self-organized honeycomb-patterned polymer films. Hexagonally arranged micro-patterns are formed in the surface of Si substrates by using the simply prepared porous polymer masks.

Experimental Part

Polystyrene (PSt, Mw ~280,000 g/mol) was purchased from Aldrich, USA. An Amphiphilic polyacrylamide derivative (**1**, Chart 1 (b), m: n = 4: 1) was synthesized by free-radical polymerization as described elsewhere[21]. Poly(vinyl alcohol)(PVA, Chart 1 (c)) was purchased from Wako Pure Chemical Industries, Ltd., Japan. Single crystalline Si substrates (resistance ≤0.02 Ωcm, semiconductor type was N, and facet was 100) were purchased from The Nilaco corporation, Japan.

The honeycomb-patterned films were prepared by casting c.a. 10 mg/mL chloroform solutions of PSt and **1** (PSt: **1** = 10: 1) on 20 x 11 cm glass substrates. The casting volume of the polymer mixture solution was c.a. 30 mL. Moist air (temperature 25 °C, relative humidity c.a. 90%) was applied to the solution surface at a flow rate of c.a. 130 L/min. The honeycomb-patterned polymer films formed following evaporation of the chloroform.

In order to separate and directly attached the porous top layer of the honeycomb-patterned films to a Si substrate, following process has been carried. To make the film surface hydrophilic, the honeycomb-patterned films were treated by UV-O_3 (OCA-150L-D, Iwasaki Electric Co., Ltd., Japan) for 10 min[22]. One wt% aqueous solution of PVA, which act as adhesion layers to Si substrates, was spin-coated on the honeycomb-patterned films (1000 rpm, 120–150 s), then the honeycomb patterned films were fixed up side down on the Si substrates. The Si substrate with the honeycomb-patterned films were annealed at 90 °C for 10 min for completely drying the PVA solution. After peeling off the dimpled bottom layer of the honeycomb-patterned films with adhesive tape (Scotch Tape, 3M, USA), excess PVA was washed out by deionized water.

Si substrates with the porous polymer masks were etched by using Inductively Coupled Plasma (ICP) dry etching equipment (SPM-200, SUMITOMO PRECISION PRODUCTS CO., LTD., Etching gas: SF_6, Passivation gas: C_4F_8). The etching and passivation processes were repeatedly carried for 1 to 10 min, respectively (Etching process: gas flow ratio of SF_6 and C_4F_8 were 50 sccm and 90 sccm, flow time was 5.5 s, Passivation process: gas flow ratio of C_4F_8 was 140 sccm, flow time was 5.0 s). After dry etching, etched Si substrates were soaked in 50% acetone aqueous solution and sonicated for 30 min for removing the masks. The surface structures of the Si substrates were determined by using a scanning electron microscope (SEM, Miniscope, Hitachi High-Technologies Corporation, Japan), a field emission scanning electron microscope (FE-SEM, Hitachi High-Technologies Corporation, Japan, V_{acc}: 7 kV, I_e: 10 μA), and atomic force microscopy (AFM, Seiko Instruments Inc., SPA-400, SPI-3800N), respectively. For removing the polymer porous masks, etched Si substrates were immersed in 50% acetone aqueous solution, and sonicated for 30 min.

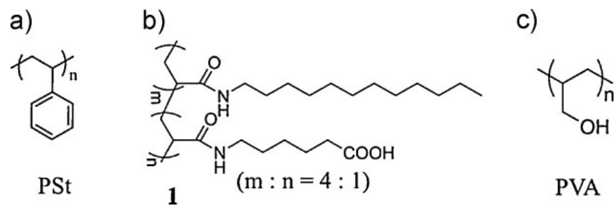

Chart 1.
Chemical Structures of (a) polystyrene (PSt), (b) Amphiphilic copolymer (1) and (c) Poly (vinyl alcohol) (PVA).

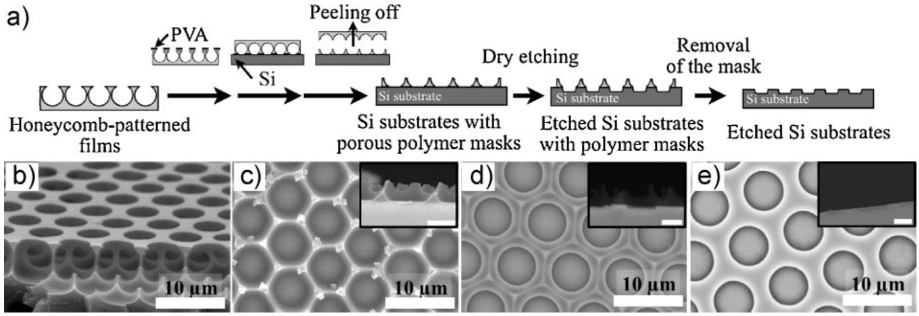

Figure 1.
(a) Preparation procedure of the structured Si substrate. SEM images of (b) the honeycomb-patterned film, (c) Si substrate with porous polymer mask, (d) Etched Si substrate with porous polymer mask (Etching time was 5 min) and (d) Etched Si substrate, respectively. Insert images show each cross-sectional view (Bars were 3 μm).

Results and Discussion

Figure 1(a) shows a schematic mask preparation and etching procedure of the etched Si substrate. The honeycomb-patterned films of PSt and **1** were prepared by casting the solution under humid conditions. The honeycomb-patterned films having double layer structures, which porous top layer and dimpled bottom layer, connected with pillars located on apexes of honeycomb hexagons (Figure 1(b)). As the prepared honeycomb-patterned films is not suitable for dry etching masks because of existence of dimpled bottom layer. Figure 1 (c) shows SEM image of the Si substrate with the porous polymer masks. Polymer mask having hexagonally arranged micro-pores and spikes-array was formed on the Si substrates. After dry etching for 5 min, the Si substrates were etched at only porous parts of the honeycomb-structured polymer mask, and polymer porous masks were still remained on the surface (Figure 1(d)). Figure 1(e) shows the etched Si substrate after removal of the polymer masks. Hexagonally arranged micro-pores were formed on the Si surface.

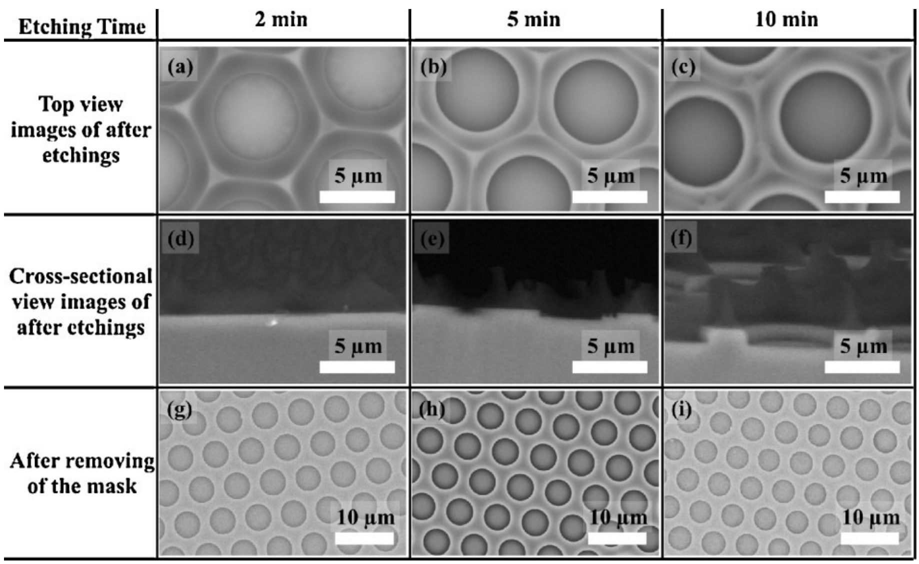

Figure 2.
SEM images of etched Si substrates (a-f) with and (g-i) without porous polymer masks, respectively.

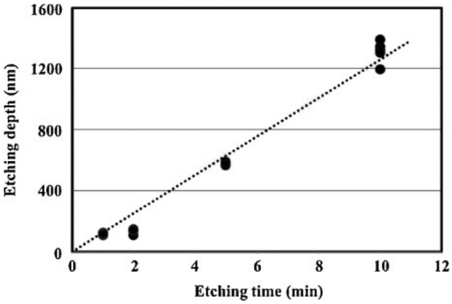

Figure 3.
Plots of the etching time and etching depth.

Figure 2 shows SEM images of etched Si substrates before and after removal of the porous polymer masks. Etching depth of Si substrates was increased with etching time. Porous polymer masks were also gradually etched, but 10 min etching was not enough to complete etching of the porous polymer masks. After sonication in 50% acetone aqueous solution, polymer masks were completely removed (Figure 2(g-i)). Pores formed at the Si surface were vertical. From results of AFM measurements, depth of Si pores was lineally increased with etching time, and etching rate was estimated to be c.a. 130 nm/min (Figure 3). This means that depth of vertically etched micro-pores can be controlled by etching time.

Conclusion

In conclusions, we prepared Si substrates having hexagonally arranged micro-pores by using self-organized porous polymer masks for dry etching. Pore sizes of honeycomb-patterned films can control from sub-micron to c.a. 30 μm, and honeycomb-patterned films can obtain A4 size. These matters also suggest this low cost mask preparation method can substitute for various masks of surface texturing. Furthermore, this demonstration is a practical example of combining top down techniques and bottom up self-organization techniques. Since wide variety of polymer patterns have been prepared by using self-organization process, many kinds of patterns are expected to use of texturing masks.

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