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Fabrication of micro-/nano-pore arrays with metal-assisted chemical etching and surface modification aiming at liquid retaining function

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Abstract

This paper discusses about structured surfaces infused with a special liquid. This approach method can eliminate limitation of self-cleaning surface with solid structure only when low surface tension liquids will be used for cleaning. Metal-assisted chemical etching produces high aspect ratio micro-/nano-pore structure on a silicon substrate and thus expected to keep much liquid in its vacant space. A pattern of islands of catalyst gold layer that is a key point was deposited using self-assembly of silica particle as a mask. The substrate was then etched with mixture of hydrofluoric acid and hydrogen peroxide. The originally hydrophilic oxide layer of silicon can be changed to hydrophobic by coating hydrophobic material. So chemical affinity of surface with retaining liquid can be improved. Finally liquid retaining function was examined. With high aspect ratio nanopore structure, the surface has durable retaining function.

Structured surface, metal-assisted chemical etching, silicon, self-assembly of monolayer (SAM), liquid retaining function

1. Introduction

Structured surfaces can afford various functions. Structured surfaces infused with a special liquid in their vacant space have been proposed with special abilities beside self-cleaning, such as oleophobicity, antifouling [1, 2]. Though the initial self-cleaning performance is good, it has the problem of short life because the liquid is easy to drop off. Thus improvement of liquid retaining function is necessary.

Metal-assisted chemical etching (MACE) is site-selective and directional etching of silicon in which noble metal works as a catalyst. To produce an ordered structure, patterning of metal layer becomes important. Sphere lithography can be used to produce a monolayer of fine particles on a substrate, a particle mask. For example, Au can be deposited through the silica particles. As a result, an array of gold islands with regular pitch can be obtained. After etching in hydrofluoric acid and hydrogen peroxide solution, micro-/nano-pore array can be obtained. Sizes of each pore and height can be controlled easily by changing the particle diameter and the etching time respectively.

The surface can be modified by self-assembled monolayer of octadecyltriclorosilane (OTS). Its low surface energy is expected to improve the structure's affinity to liquid that should be infused. However such modification has not been necessarily discussed because of the difficulty in the deposition on high aspect ratio structures. Formation of hydroxyl groups on structure is essential to produce high coverage and uniform OTS layer. Acid treatment can make rich hydroxyl surface but high aspect ratio structure can be easily deformed due to meniscus attraction of the liquid.

This paper aims to make clear the applicability of the combination of sphere lithography and MACE to fabricate micro-/nano-pore structures. The suitable conditions for surface modification of these structures will be made clear. Then the effects of structural design and surface modification on liquid retaining ability will also be discussed.

2. Background of liquid retaining function

Various microscopic structures have been proposed to retain special liquid in their vacant spaces. Obviously the life of surface depend on how much liquid they can contain and how strong they can hold. Porous structure can play as reservoir to keep much liquid [1]. High aspect ratio structure is a good idea. And uniform low surface energy coating is necessary to produce high chemical affinity (Fig. 1).

Requirements for the liquid are low surface energy, low evaporation that ensure energy balance (the retaining liquid is not displaced by cleaning liquid), long life respectively. Immiscibility of the liquid is also essential.

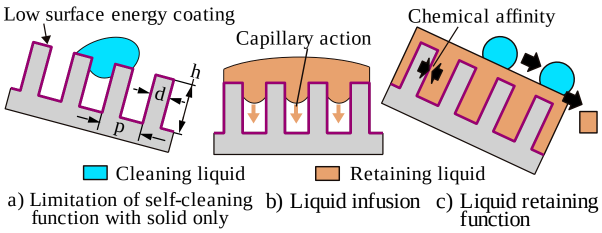

Figure 1. Background of liquid retaining function

3. Fabrication of fine structures

Figure 2a-c shows a schematic of fabrication process and corresponding scanning electron microscope (SEM) images. Monolayer of silica particles can be self-assembled easily by dip coating method [3]. After Au deposition, the substrate was etched in solution of HF and H_2O_2. Well-ordered micro-/nano-pore arrays were obtained with hexagonal pattern. The pore diameters correspond with that of the particles (ϕ1 µm and ϕ10 µm). Figure 2d show the correlation between etching time and etched depth when using ϕ1 µm particles as a mask. The etching rate was found around 0.7 µm/min. Aspect ratio (AR) as high as 30 was achieved. Table 1 shows the experimental conditions.

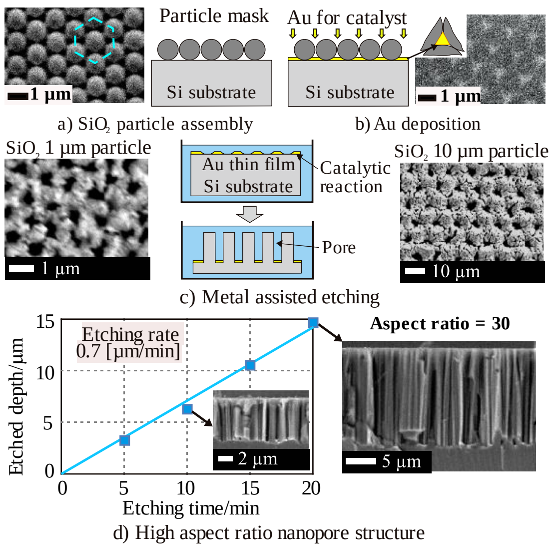

Figure 2. High aspect ratio structure fabricated by sphere lithography and MACE

Table 1. Experimental condition.

Substrate	Material /size	Silicon, 10 mm × 10 mm
Self-assembly	Suspension	Water, Silica ϕ 1 μm, 10wt%
	Draw up speed/angle	0.1 mm/s – 1 mm/s 45° – 60°
Au film thickness		20 nm
MACE condition	Etchant	$HF:H_2O_2:C_2H_5OH$ = 3:1:6
	Temperature	20 °C
	Etching time	5, 10, 15, 20 min
Drying conditon		Baking at 60 °C

4. Liquid retaining function

The originally hydrophilic oxide layer of silicon can be changed to hydrophobic by modifying with OTS. Figure 3 shows wettability of the modified surface. Perfluoropolyether was chosen because of its low surface energy, low evaporation and immiscibility. The different appearances of surfaces with and without liquid infusion when dipping in water medium were shown in figure 3a, b. The reason is air trap layer in case solid structure. Figure 3c shows the limitation of solid surface when using diethylene glycol (DEG, surface tension = 44.80 mN/m [4]). DEG drops can move only on liquid infused surface.

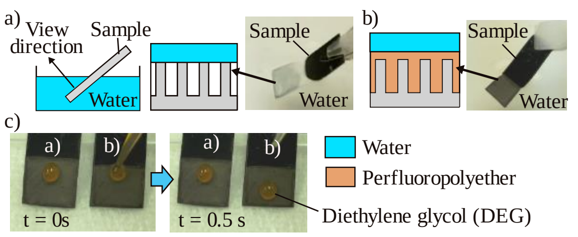

Figure 3. Liquid retaining surface via OTS coating of nanopore structure and its wettability

4.1. Surface modification of high aspect ratio nanostructure

Figure 4 shows schematic and result of OTS deposition. Piranha treatment was used to produce hydroxyl groups on structure. The important issues is deformation of fine structure due to meniscus attraction when using high surface tension solution and fast drying. Here we used ethanol, low surface tension liquid, as rinse solution and drying speed was controlled by hot plate. Result is no deformation of high AR nanostructure (Fig. 4b, top view of structure). The substrate was then dipped into OTS solution in certain time and exceeded OTS was remove by toluene. Effect of dipping time on contact angle of the substrate is shown in figure 4d. Highest contact angle was obtained with 40 minute dipping time. Table 2 shows the detail conditions.

Table 2. Experimental condition.

Hydroxyl formation	Piranha solution	$H_2SO_4:H_2O_2$ = 3:1
	Time/temperature	2 hour/70 °C
	Rinsing	C_2H_5OH, H_2O
	Drying	60 °C
OTS deposition	OTS solution	OTS 3 wt%, Toluene
	Time	20 min – 480 min
	Washing solution	Toluene

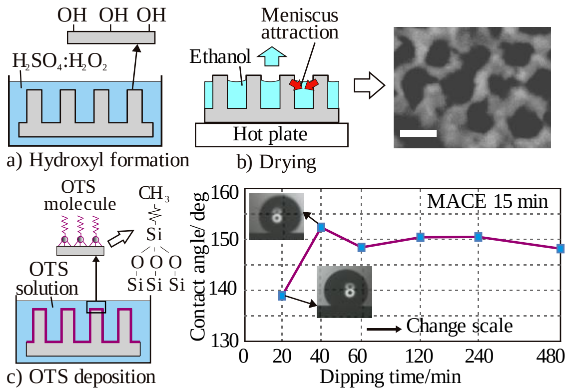

Figure 4. OTS deposition on high aspect ratio nanopore structure

4.2. Evaluation for durability of retaining function

Durability of retaining function against liquid dash was investigated by residue of liquid on the surface after number of dash. Figure 5 shows this correlation with respect to different height of structure. Shallow structure has short life. With high AR nanostructure, the infused liquid was held strictly. It has good durability with no residue of DEG after larger number of dash.

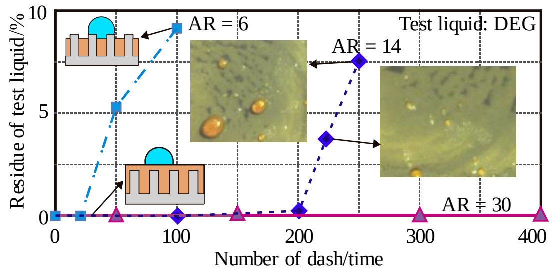

Figure 5. Residue of DEG versus number of dash

5. Conclusion and future work

Combination of sphere lithography and MACE can produce well-ordered, high AR nanopore arrays. After surface modification, the function of these structure was investigated. High AR structures can keep much liquid strictly so durable retaining function and self-cleaning function was achieved. Evaluation of the liquid penetration depth is one of the future problems. Other one is the scale extension.

References

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