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Metal-assisted chemical etching of silicon with deposited Ag nanoparticles aiming for functional surfaces

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Abstract
Metal-assisted chemical etching is one of the anisotropic etching processes of silicon. The major characteristic is site-selective process due to catalytic reaction at the contact point between noble metal and silicon, and a high-aspect ratio can be obtained. This paper aims to make clear the possibility of the metal nanoparticle deposition and its effect on the etched profiles including an application to the production of hydrophobic surfaces. Suspension that contains silver-nanoparticles was dropped on a silicon substrate. By changing the particle concentration, the coverage of the particles could be controlled. Then, the effect of etchant condition, mixture of fluoric acid and hydrogen peroxide water, on the etching rate and final profile was made clear. It was found that an array of nanopores or nanopillars were produced and the aspect ratio reached about 40. Since steep cross-sectional profile can change the wettability of the surface, its effect on the contact angle of water droplet was examined. By applying nanostructure on the substrate, the contact angle increased up to 126 degrees while that without structure was 58 degrees.

Metal-assisted chemical etching, silicon, structured surface, aspect ratio, wettability

1. Introduction

Metal assisted chemical etching (MacEtch) can produce high aspect ratio structures on a silicon substrate [1, 2]. The principle is the site-selective etching at the interface where noble metal contacts with the silicon as a catalyst [3]. So far, gold or silver films were deposited on a silicon substrate with the specified pattern and nanopillars or columns were produced [3].

Fine particles can be easily assembled on a substrate using self-organizing process. Regular assembly of metal particles can produce regular structure or texture of silicon with MacEtch. However there were little studies that investigate the variation or controllability of the profile. Also the number of studies that correlate such structure with applications is limited [4].

This paper aims to make clear the applicability of metal particle assembly to MacEtch patterning. In the latter part, the wettability of the structured surface will be discussed.

2. Basic properties of Ag particle deposition and MacEtch

Figure 1 shows a schematics of the top-views of the particles deposited on a substrate and the cross sectional views after MacEtch. The effect of the coverage variation is also shown. The contact points of the particles are selectively etched and deep pores can be produced. The pore diameter correspond with that of the particles. If the coverage of the particle is low, pores distribute sparsely. With the increase in the coverage of the particles, the final profile becomes pillar array. If the coverage increases further and aggregate becomes multilayer, the pillar density decreases and the final profile will become complex. Thus, the control of the coverage and its uniformity, including the number of layers, will be the key factors in obtaining well-structured texture.

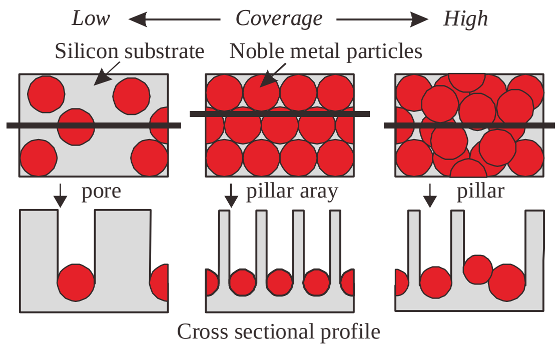

Figure 1. Characteristic of metal assisted chemical etching and the effect of metal particle coverage.

Fine particles are often available as an aqueous suspension. The simplest deposition method is dropping it on a substrate. Dropping a suspension that contains particles, then aggregated structures remains on the substrate after evaporation of water. Ideally, packed structure of the particles can be obtained easily. Table 1 shows the experimental conditions. The nominal diameter of the Ag particle was ϕ150nm. Figure 2 shows the observation results of the particles with a scanning electron microscope (SEM). The effect of the concentration of suspension can be seen from the figure, that is, the coverage increased with the increase in the concentration. However, it was also found that the particle aggregate size was not constant but varies up to micron level and multi-layered.

Table 1. Deposition condition of Ag particles.

Substrate		Silicon (100)
Metal particle suspension	Particles	Ag, ϕ150 nm
	Concentration	0.1, 0,2, 0.3, 0.5, 1 wt%
	Solvent	H_2O
	Drop volume	50 μl

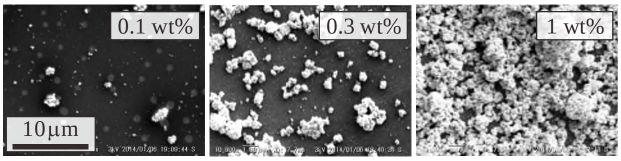

Figure 2. Deposited Ag particles and the effect of the concentration.

Figure 3 summarizes the effect of the Ag particle concentration on the coverage that was calculated by using an image processing software. It was found that the coverage increased linearly with the concentration, which suggests the controllability of coverage by adjusting the concentration.

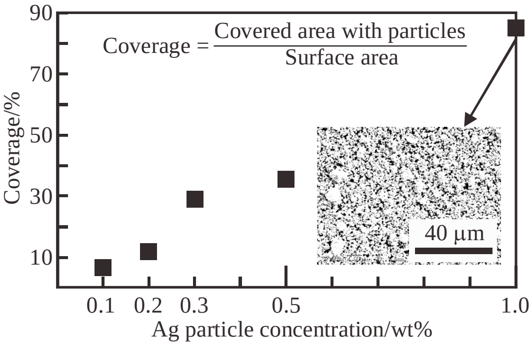

Figure 3. Relationship between Ag particle concentration and coverage.

Etching experiments were carried out according to the conditions in Table 2. Mixture of fluoric acid and hydrogen peroxide is generally used as the etchant. In this study, this solution was diluted aiming at the improvement of the etching depth controllability. Average etching rate of the diluted was 860 nm/min while that without dilution was fast as 10 μm/min.

Figure 4 shows the cross-sectional observation of etched results, comparing the effect of Ag particle concentration. High aspect ratio profiles were obtained. However, the maximum depth decreased with the increase in the concentration. In addition, the etching depth changed with the lateral position while deposited metal film produces constant depth [1]. The causes of the depth fluctuation is considered as the difference in the aggregation size as shown in Fig. 2.

Figure 5 shows the relationship between the concentration and the average etching depth. When the concentration is low, the depth increases and thus pores becomes sparse and deeper. Attention should be paid when low concentration is applied.

Properties of MacEtch were made clear. It was also found the uniformities of aggregation size and distribution are crucial to obtain constant pore/pillar diameter, pitch and depth.

3. Extension of the deposition area

Former results suggest the controllability of not only pore/pillar concentration but its depth over a wide range. However the structuring area is limited as far as dropping method is applied. To extend of the structuring area, spray method was tried. Using ultrasonic spray, mist of the suspension was produced and guided onto a silicon substrate that was put on a hotplate to speed up the evaporation of water. Using this apparatus, the structuring area was extended to ϕ100 mm. However, the coverage was limited up to 5 %. Further remodelling of the setup is necessary.

Table 2 Metal assisted chemical etching conditions.

Composition	$HF:H_2O_2:H_2O$ = 3:1:12
Etching time	30 minutes
Temperature	30 degrees

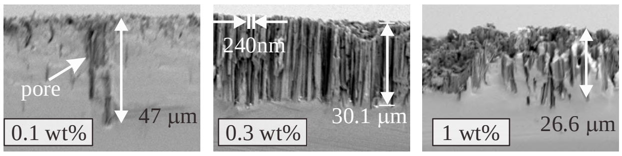

Figure 4. Cross-sectional observation of the etched profile with a SEM and the effect of Ag particle concentration.

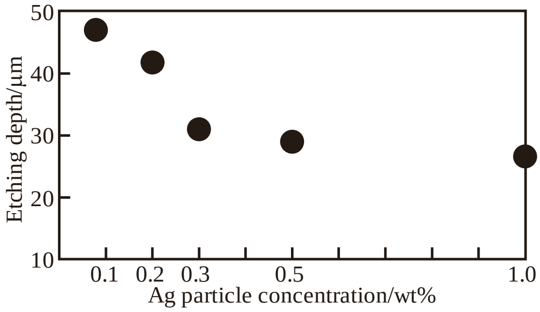

Figure 5. Effect of Ag particle concentration on etching depth.

4. Control of the wettability as a functionality

Figure 6 shows the effect of structural aspect ratio on the contact angle of water droplet. With the increase in the aspect ratio, the contact angle increased continuously. It was confirmed that hydrophilic silicon surface was changed to hydrophobic. The increase in the contact angle is often attributed to the air trap between the structures. Thus, the contact angle change discontinuously in general. Further investigation is necessary.

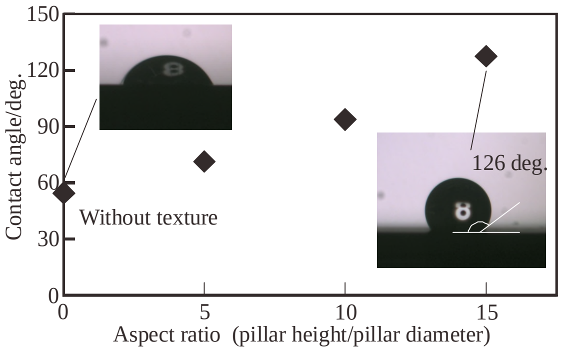

Figure 6. Effect of aspect ratio on contact angle of water droplet.

5. Conclusions

Basic properties of metal-assisted chemical etching of silicon with Ag nanoparticle catalyst were made clear. Various structures with different pattern and depth were obtained by changing the deposition condition. Finally, wettability control was demonstrated and hydrophilic substrate was changed to hydrophobic. The improvement of particle dispersiveness is one of the future problems.

References

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