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Metal Assisted Chemical Etching

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1. Introduction

Metal Assisted Chemical Etching has been investigated to fabricate silicon (Si) nanostructure arrays (nanowires and/or nanopores) with diameters of 5 nm to 1 µm, using its simple and low cost process (Z. Huang et al., Adv. Mater. 23, 285 (2011)). Figure 1 shows a redox scheme of Metal Assisted Chemical Etching, which preferentially etches the Si beneath a noble metal in a mixed solution of hydrogen fluoride (HF) and hydrogen peroxide (H₂O₂). As indicated in figure 1, the holes are preferentially generated on the noble metal by the reduction of H₂O₂, and are injected into the Si substrate through the interface between the Si and noble metal. The oxidized Si atoms dissolve into the HF solution, and react with HF to produce silicon hexafluoride ion (SiF₆²⁻). The etch rate of the Si substrate with the noble metal on its surface is much faster than that without the noble metal, due to the catalytic activity of the noble metal.

The goal of this project is to confirm if Metal Assisted Chemical Etching is useful to fabricate a micro-device. Figure 2 shows a process flow of Metal Assisted Chemical Etching of this report.

2. Experimental Section

A. UV lithography using SUSS MicroTec MA6 Gen3 Mask Aligner

A Si wafer was sonicated in acetone and isopropyl alcohol (IPA) for 5 min each. Hexamethyldisilazane (HMDS) was vapor primed on the Si wafer as an adhesion promoter, using YES oven (Yield Engineering Systems), followed by spin-coating positive photoresist S1818 (Microchem) at 5500 rpm for 30 sec. The photoresist film was baked at 115°C for 5 min on a hot plate, and was exposed to 405 nm UV light with the power of 150mJ/cm², using SUSS MicroTec MA6 Gen3 Mask Aligner. The exposed photoresist film was developed in MF319 (Microchem) for 60 sec, and was rinsed with de-ionized (DI) water. The sample was then dried using a nitrogen gun.

B. Au Deposition

A 5 nm thick Au film was deposited onto the developed photoresist film under the base pressure of ~8.0 x 10⁻⁸ Torr, using load lock PVD-75 e-beam evaporator (Kurt J. Lesker). The deposition rate was 2.0 Å/sec.

C. Lift-off

The photoresist film along with the Au film deposited on top of it was lifted-off by sonication in Remover PG at 60 °C, leaving behind only the Au film deposited directly on the Si wafer.
D. Metal Assisted Chemical Etching

The Si wafer with the 5 nm thick Au pattern on its surface was immersed in a 1:1:1 (v/v) mixture of ethanol, HF (49 wt%), and H₂O₂ (30 wt%) for 2, 3, and 30 min. Then, the sample was rinsed with DI water, and dried using a nitrogen gun.

3. Results and discussion

Figure 3 shows SEM images of 50 µm x 50 µm square and 5 nm thick Au films with the off-metal spaces of 2.5 and 3.0 µm after Metal Assisted Chemical Etching. The samples were immersed in the etching solution for (a) and (b) 2 min, (c) 3 min, and (d) 30 min, respectively. Figures 3(a) and 3(b) are the same sample with different contrasts.

![SEM images of 50 µm x 50 µm square and 5 nm thick Au film with the spaces of 2.5 and 3.0 µm after Metal Assisted Chemical Etching.](image)

Figure 3. SEM images of 50 µm x 50 µm square and 5 nm thick Au film with the spaces of 2.5 and 3.0 µm after Metal Assisted Chemical Etching; (a) and (b) 2 min etching, (c) 3 min etching, and (d) 30 min etching, respectively. Figure 3(a) and 3(b) are the same sample with different contrasts.
As can be seen in figure 3, the 2.5 µm off-metal space between the blocks is not etched for 2 min etching, but Au fragments start to etch the space for 3 min etching. The off-metal space is completely etched by Au fragments broken from the on-metal area during 30 min etching. Furthermore, the area of the porous structure on the Au films is increased with increasing the etching time.

Figure 4 displays higher magnification SEM images of the 5 nm thick Au film after 2 min etching. Figure 4(a) shows that the Au films collapse due to the dissolving the Si atoms, leaving the Au fragments on the surface. Since the 1.5-2.0 nm thick native oxide of the Si substrate is not removed before the Au deposition, the HF molecules must diffuse through the Au film to dissolve the native oxide. It is also strongly suggested that the by-product SiF$_6^{2-}$ molecules diffuse through the Au film collapsed after the reaction with HF. These suggest that the Au fragments should be broken by the mass transfer through the Au film during the long time etching, and should etch the off-metal area randomly. On the other hand, figure 4(b) indicates that some Au fragments smaller than ~1 µm etch the deeper Si.

![Figure 4. SEM images of the 5 nm Au film after 2 min etching.](image)

Figure 5 shows SEM images of (a) 2.4 µm width lines and (b) 20 µm width lines of the 5 nm thick Au films after 30 min etching, respectively. Figure 5(a) indicates that the 3.6 µm width off-metal lines, next to the 2.5 µm width on-metal lines, are not etched seriously by the Au fragments. On the other hand, figure 5(b) displays that the 20 µm width off-metal lines, next to the 20 µm width on-metal lines, are heavily etched by the Au fragments, as the etching behavior in figure 3(d). This implies that the Au fragments on the 2.4 µm width on-metal lines are not broken during the 30 min etching, but etch the Si vertically, although the porous surface is still observed in figure 5(a). It is speculated that in the small on-metal area, the reagent and byproduct diffuse along the interface between the noble metal and the Si substrate (Z. Huang et al., Adv. Mater. 23, 285 (2011)). It is assumed that the mass transfer along the interface in the 2.4 µm width on-metal lines helps to keep the Au fragments on the surface, so that the 3.6 µm width off-metal lines are not etched seriously by the Au fragments.
4. Summary
Metal Assisted Chemical Etching was performed in QNF to confirm if the etching was useful to fabricate a micro-device. The etching was successful, but left the porous structure in the on-metal area. Furthermore, the off-metal area next to the large on-metal area was heavily etched by the Au fragments broken from the on-metal area due to the mass transfer through the Au film. On the other hand, the off-metal area next to the small (2.5 µm) on-metal area was not etched seriously due to the mass transfer along the interface between the noble metal and the Si substrate. As a result, it is concluded that Metal Assisted Chemical Etching is unfit for fabrication of the micro-device.

Figure 5. SEM images of (a) 2.4 µm width lines and (b) 20 µm width lines of 5 nm thick Au films after 30 min etching.