Study of improvement in silicon bulk micromachining by metal assisted chemical etching

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Abstract. Ensuring the integrity and uniformity of the fabricated structure is critical for silicon bulk micromachining. Our research demonstrates an efficient and low-cost method for silicon bulk micromachining by metal-assisted chemical etching (MACE). The integrity and uniformity of the etched structures are greatly improved by the utilization of ethanol as the solvent instead of water. Our research helps to understand the mechanism of MACE, and can provide new ideas for the further study of morphology control of silicon block micromachining using MACE.

1. Introduction
In the past few decades, the microstructure of silicon (Si) has been widely used in many fields, including micro-electromechanical systems (MEMS) [1], optoelectronics [2], energy conversion [3], and gas sensors [4], etc. Among these applications, some microstructures with very large lateral and vertical dimensions of tens to hundreds of microns need to be fabricated by bulk micromachining. Traditional silicon bulk micromachining is usually realized by dry etching, such as deep reactive ion etching (DRIE) [5]. However, these methods usually require high vacuum environment and expensive equipment, along with complicated processes and limited etching depth.

Metal assisted chemical etching (MACE), as a new anisotropic wet etching method, is getting ever increasing attention in the preparation of silicon microstructures with high aspect ratios [6,7]. A typical MACE process mainly includes the following two reaction equations [8].

\begin{align}
2H^+ + H_2O_2 &\xrightarrow{\text{noble metal}} 2H_2O + 2h^+ \\
Si + 4HF_2 + 2h^- &\rightarrow SiF_6^{2-} + 2HF + H_2(g)
\end{align}

The noble metals act as catalysts, including but not limited to Au, Ag and Pt. On the surface of the catalytic metal film, hydrogen peroxide (H$_2$O$_2$) in the etching solution is reduced and a large number
of holes are then injected into the silicon under the catalytic metal film. The silicon oxidized by the holes is dissolved by hydrofluoric acid (HF) in the etching solution.

In this paper, we reported an efficient and low-cost wet etching method for bulk micromachining of silicon by MACE. We prepared two kinds of etchant with deionized water and ethanol as solvents, respectively. The morphology of the catalytic metal film after etching in these two kinds of etchant were examined. The integrity and uniformity of the etched structures obtained by the two kinds of etchant are compared to illustrate the improvement in silicon bulk micromachining by the utilization of ethanol instead of water.

2. Experimental details

2.1. Patterning of samples

Single-side polished, N-type, <100> CZ-grown silicon wafers (Buntoo Industrial, Ltd) with resistivity of 1–10 Ω·cm were used as the samples. H₂O₂ and Au were used as the oxidant and the metal catalyst, respectively. Figure 1 illustrates the experimental procedure for the metal assisted chemical etching. Firstly, the samples were pretreated with standard RCA clean (85°C 1:1:5 NH₄OH:H₂O₂:H₂O solution for 10 min; de-ionized water (DI) rinse; 1:10 HF: H₂O for 1 min; DI rinse; 85°C 1:1:6 HCl: H₂O₂:H₂O solution for 10 min; DI rinse), HF dip, and 150°C hexamethyldisilazane (HMDS) vapor soak. A 1.7-μm-thick layer of AZ 1500 (20cp) photoresist (AZ Electronic Materials) was spin-coated onto the silicon samples and soft baked at 90°C for 90 s. The target patterns were transferred to the photoresist on silicon substrates using a URE-2000/35 (Chengdu Institute of Optoelectronic, CAS, and China) mask aligner. Following a 90 s post bake at 100°C hotplate, the substrates were developed for 12 s at 2.38% tetramethylammonium hydroxide (TMAH), followed immediately with a DI rinse and dried with N₂ flow. The patterned substrates were finally hard baked at 110°C for another 90 s. A 5 nm Ti was deposited on the silicon substrate as a bonding layer by magnetron sputtering. After that, a 16 nm Au layer was evaporated using an electron beam evaporator and followed by a lift-off process.

2.2. Etching of samples

The sliced samples were placed into the etchant ([HF] = 1.92 M and [H₂O₂] = 2.88 M, 4.3 mL 40% HF and 14.4 mL 30% H₂O₂ were mixed and DI or ethanol was added to reach a total volume of 50 ml) and MACE was performed. The metal film sunk into the trench was removed in aqua regia after the etching. Finally, the samples were rinsed in DI water, dried, and cleaved for the morphological observation, which was carried out in a Zeiss Ultra Plus field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 5 kV.

![Figure 1](image_url)

**Figure 1.** Schematic diagram of experimental procedures for the metal assisted chemical etching: (a) wafer cleaning; (b) spin-coating of photoresist; (c) UV exposure and development; (d) magnetron sputtering of 5 nm Ti and e-beam evaporation of 16 nm Au; (e) lift-off; and (f) etching.
3. Results and discussions

It can be seen from Fig. 2(a) that after etching in the HF/H$_2$O$_2$/H$_2$O etchant for 1 hour, part of the Au film appears incomplete in some etched structure. It has fallen off from the silicon substrate or curled up in the edge of the Au film. However, after being etched in HF/H$_2$O$_2$/ethanol etchant for 10 hours, most of the Au film in the etched structure of the sample still maintained a close contact with the silicon substrate (Fig. 2(b)).

**Figure 2.** Top view of the SEM images of samples after etching in (a) HF/H$_2$O$_2$/H$_2$O etchant for 1 hour, and (b) HF/H$_2$O$_2$/ethanol etchant for 10 hours, respectively.

It can be known from the MACE etching principle mentioned above that the etching reaction between the etching solution and silicon occurs only in the area covered by the catalytic metal film. Therefore, the morphology of the catalytic metal film determines the etched structure, which are obvious in the etching results shown in Fig.3. Comparing with the SEM image of the sample after being etched in the HF/H$_2$O$_2$/H$_2$O etchant (Fig.3 (a)), it can be found that the sidewall of the trench structure obtained by etching in the HF/H$_2$O$_2$/ethanol etchant is more vertical and the floor of trench is smoother (Fig.3 (a)). In addition, it can be found in Fig.3 (b) that the etching width of the etching structure obtained in the HF/H$_2$O$_2$/ethanol etchant varied from tens of micrometers to hundreds of micrometers, which confirms the capability of MACE using ethanol as the solvent in the etchant for silicon bulk micromachining.

**Figure 3.** SEM images of 20° tilted view of samples after etching in (a) HF/H$_2$O$_2$/H$_2$O etchant for 1 hour, and (b) HF/H$_2$O$_2$/ethanol etchant for 10 hours, respectively.

To explain that the uniformity was much improved by the addition of ethanol, Khang et al. [9] proposed that ethanol has low surface tension of 22.4 mN/m and the addition of ethanol as co-solvent can thus form a more complete wetting of etchant on the Ag/Au bilayer catalyst surface. It helps to
prevent the hydrogen bubble from attaching to the catalyst surface during the etching. However, it cannot explain the phenomenon for the decreased etch rate in the etchant with ethanol as co-solvent, which was observed in our experiment.

As shown in Fig. 4, the etched depth of the trench after etching for one hour in the HF/H$_2$O$_2$/H$_2$O etchant is 31 μm with an etching rate of 31 μm/h. However, the etched depth of the trench after etching in HF/H$_2$O$_2$/ethanol for 10 hours in the etching solution is only 66 μm with an etching rate of 6.6 μm/h. The etch rate in etchant with ethanol as co-solvent was significantly reduced. However, there is still no reasonable explanation for this phenomenon and further study is needed.

![Figure 4](image.png)

**Figure 4.** Cross-sectional SEM images of samples after etching in (a) HF/H$_2$O$_2$/H$_2$O etchant for 1 hour, and (b) HF/ H$_2$O$_2$/ethanol etchant for 10 hours, respectively.

### 4. Conclusion

To summarize, we verified that the integrity of bulk micromachining of silicon by metal assisted chemical etching has been greatly improved after the utilization of ethanol instead of DI water as the solvent of etching solution. We found that compared with the case where the catalytic metal film is very easy to fall off from the substrate and drift into the etchant, the catalytic metal film sank uniformly to stay close contact with the silicon substrate. The gold film remained intact even after 10 hours etching process in the etchant with ethanol as co-solvent. The versatility to etch a wide variety of structures with vertical and smooth sidewalls uniformly also gives the silicon bulk micromachining using MACE great potential in applications such as MEMS devices.

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