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Fabrication of Very-High-Aspect-Ratio Microstructures in Complex Patterns by Photo-Electrochemical Etching

Guangyi Sun, Xin Zhao, and Chang-Jin "CJ" Kim

Abstract— We have fabricated very-high-aspect-ratio (VHAR) silicon and metal microstructures in complex geometric patterns. The recently developed surfactant-added tetramethylammonium hydroxide (TMAH) etching allows the formation of V-grooves in any pattern, i.e., not limited by the crystal direction, on a silicon surface. As the resulting sharp pits allow very deep photo-electrochemical (PEC) etching, VHAR silicon microstructures (4 µm-wide and over 300 µm-deep trenches) are successfully fabricated in complex patterns (spiral and zigzag demonstrated), overcoming the prevailing limitations of simple pores and straight trenches. Furthermore, by filling the VHAR silicon mold with nickel and removing the silicon, HAR metal microstructures of complex patterns are also obtained. These VHAR microstructures in complex patterns, which are structurally much stronger than the simple posts and straight plates, overcome the stiction problem even when densely populated.

Index Terms—Very-high-aspect-ratio (VHAR), high-aspect-ratio (HAR), surfactant-added TMAH, photo-electrochemical (PEC) etching, vacuum degassing, electroplating.

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I. INTRODUCTION

Microstructures of high-aspect-ratio (HAR) are important for microelectromechanical systems (MEMS) because they are critical for many important applications [1]–[8]. Since the late 1990s, the workhorse for HAR fabrication has been the deep reactive ion etching (DRIE) of silicon. As a highly anisotropic dry etching process, DRIE is used to create HAR holes and trenches in wafers, with aspect ratios (depth-to-width) of over 10:1 but usually below 40:1 [7], [8]. While requiring expensive tooling, DRIE still has some inherent deficiencies. For example, the overall etching rate of a DRIE process is not only dependent on the process parameters, e.g., power, pressure, cycling between etch and deposition, but also dependent on the etched trench width or hole diameter, i.e., lag effect. Also, a typical DRIE creates sidewalls with microscopic scallops rather than a smooth surface.

Another promising process for HAR fabrication is photo-electrochemical (PEC) etching of silicon. As a highly anisotropic wet etching process, PEC etching has traditionally been used to create an array of HAR pores in silicon wafers, with aspect ratios well over 10:1 and often 100:1 [9]–[11]. Recently, by improving the PEC etching of silicon, our lab has not only increased the aspect ratio of the pores to 120:1 – to the range of a very-high-aspect-ratio (VHAR) – but also established straight trenches as a new type of HAR microstructures PEC etching can create [12]. In comparison with the DRIE process, PEC etching can produce much higher aspect ratio holes and trenches of a smooth sidewall with uniform etching depth and etch rate. However, the PEC etching has not been widely used mostly because of its severe restrictions in the etch patterns. Unlike DRIE process, which uses a regular photolithographic mask to define the etching and non-etching area, PEC etching requires sharp pits, which serve as nucleation sites to etch deep into the silicon wafer. The sharp pits have mostly been formed by wet anisotropic etching, such as potassium hydroxide (KOH) and tetramethylammonium hydroxide (TMAH). As a result, on a typical (100)-type silicon wafer, any patterns not aligned to a <110> direction, especially convex corners, would suffer from an undercut during the sharp-pit etching. Although attempts have been made to overcome this restriction of pattern orientation by creating the initial pits in an arbitrary pattern using an isotropic wet etchant (e.g., HNA) or reactive ion etching (RIE) [13]–[15], the PEC etching starting with

these not-so-sharp pits suffered from branches and non-uniform etching depth, limiting the aspect ratio far below what a PEC etching with sharp pits can produce.

Recently, the Sato group at Nagoya University has reported that a small amount of surfactant (e.g., Triton X-100 $(C_{14}H_{22}O(C_{2}H_{4}O)_{n}, n=9-10)$) added to TMAH can significantly suppress the undercut in all non-<110> directions [16]–[18]. Free from the undercut, the modified TMAH can anisotropically etch an arbitrary pattern with a minimal distortion. Most importantly for our interest in PEC etching, the pits of the arbitrary patterns made by this modified TMAH are also sharp.

In this report, by combining Sato's undercut-free TMAH etching process [16]–[18] with our recent PEC etching process [12], we develop fabrication of VHAR microstructures in complex patterns not bound by the crystal directions of silicon wafer. First, we define the initial sharp pits of arbitrary orientations using the surfactant-added TMAH solution. Then, starting from these sharp pits, we tune the PEC etching to produce a VHAR silicon mold with 4 µm-wide and 4 µm-spaced trenches over 300 µm deep. Utilizing the vacuum degassing-assisted electroplating technique [12] to fill the VHAR trenches with a metal and removing the silicon mold away by XeF₂ etching, we subsequently obtain micro metal structures of various shapes not bounded by silicon crystal directions. Building on the preliminary results in [19], here we report additional studies and technical data, such as: the effect of sharp pits on PEC etching of arbitrary patterns; the optimization of PEC etching of silicon structures; the process of vacuum-degassed electroplating; and the advantages of the HAR microstructures in complex patterns. Table I compares this work with the existing HAR fabrication techniques in a summarized fashion.

II. FABRICATION

The overall fabrication process for the PEC-etching-based VHAR silicon structures and metal structures of non-<110> orientation is schematically described in Fig. 1, which shows four principal steps: sharp pits formation

(Fig. 1(a)), PEC etching of silicon (Fig. 1(b)), metal filling (Fig. 1(c)), and removal of silicon (Fig. 1(d)). The first main step (Fig. 1(a)) is to form the sharp pits on a silicon surface needed to start the subsequent PEC etching. So far, the initial sharp pits for PEC etching have mostly been prepared by KOH or TMAH etching, both of which are crystalline dependent and cannot produce arbitrary patterns because convex corners and curved edges would be significantly undercut. As a result, the PEC-etched geometry is typically restricted to pores and straight trenches. A few exceptions exist in which silicon structures in a curved pattern were obtained by PEC etching. In [13]-[15], an isotropic silicon etchant (a mixture of hydrofluoric, nitric, and acetic acid, or HNA) and reactive ion etching (RIE) were used to produce the initial pits for PEC etching. Trenches of curved and complex shapes were demonstrated. However, unlike the anisotropic alkaline wet etching by KOH or TMAH, neither HNA nor RIE can form sharp pits, resulting in branches and limited aspect ratio (below 10:1). We overcome this problem by adding a small amount of surfactant Triton X-100 to TMAH [16]-[18] and following additional technical details (i.e., etching time control and no agitation) reported in [20]. Using an N-type (100) silicon wafer with a resistivity of 40-60 Ω cm, we started by depositing 500 nm SiO₂ in a STS plasma-enhanced chemical vapor deposition (PECVD) system. An array of various patterns with $\sim 4 \mu m$ line width and $\sim 4 \mu m$ spacing, i.e., 8 μm pitch was then transferred to the SiO_2 layer by photolithography and one 90 s dry etching in Ulvac NLD-570 glass etcher. This was followed by a ~ 20 s etching in buffered oxide etchant (BOE). The patterned SiO₂ served as the etching mask in surfactant-added TMAH. Following the recipe for a moderate etching rate to <100> and a minimal undercutting to non-<110> directions [16]-[18] the silicon was then etched in 25 wt% TMAH in water with 0.1% v/v Triton X-100 surfactant (laboratory grade, Sigma-Aldrich) at 60 °C for 24 min to form the sharp pits, which would serve as the nucleation sites for the subsequent PEC etching. A cylindrical Teflon beaker, containing the etchant, was kept inside a water bath to maintain the temperature.

After removing the remaining PECVD SiO₂ residue with BOE, the second main step is the PEC etching, which started on a 2 cm-diameter circular area (i.e., $\sim 3 \text{ cm}^2$) of silicon (Fig. 1(b)); the processing area is dictated by the etching apparatus. The silicon was etched in 4 wt% hydrofluoric acid (HF) (21 ml of 49% HF and 279 mL of deionized (DI) water) at room temperature while illuminating the backside with a near-infrared (870 nm

wavelength) high-power light source (Marubeni America Corporation). A few droplets of a wetting agent (Kodak Foto-Flo) were added to the electrolyte to help remove the hydrogen bubbles generated during the etching, which is very important for VHAR etching. The etching current density and bias voltage were independently kept constant at 12 mA/cm² and 3 V, respectively. After etching to a desirable depth into the silicon, the trenches were opened from the backside by DRIE.

To prepare for the electroplating (Fig. 1(c)), the PEC-etched silicon mold was first covered with a 2000 Å SiO₂ by thermal oxidation to electrically isolate the silicon surface during the subsequent metallization and prevent the bulk silicon from getting electroplated. Next, to seal the openings on the backside of the silicon mold, a Ti/Ni (100 Å / 1000 Å) seed layer was evaporated in an e-beam evaporation system (CHA Mark 40), followed by electroplating \sim 50 µm-thick nickel at 5 mAh/cm² in a plating solution (Technic, Inc.) with a nickel sheet as the counter electrode. This nickel layer then served as the seed layer for the subsequent nickel electroplating step to fill up the VHAR silicon mold. As reported in [12], a regular electroplating process cannot fill the VHAR trenches successfully because it is practically impossible to completely eliminate the hydrogen gas from such deep and narrow trenches. The trapped hydrogen introduces voids in the metal or even blocks the growth of the metal. To remove the initially trapped air when the silicon mold was immersed in the plating solution, the plating bath was evacuated and vented once before the electroplating started. On the other hand, to remove the hydrogen accumulated during the electroplating, the plating bath was evacuated and vented periodically, e.g., hourly. By using this technique of vacuum degassing-assisted electroplating, we were able to fill the VHAR mold with a metal without introducing any defects.

Eventually, to obtain the freestanding micro VHAR metal structures (Fig. 1(d)), the silicon molds were removed by a gas-phase XeF_2 etch at 3000 mTorr for ~1 hour. The thin SiO₂ surrounding the metal sidewalls was also removed during the XeF_2 etching, utilizing the poor adhesion to the metal surface and non-negligible etching in XeF_2 .

III. RESULTS AND DISCUSSION

A. Initial pits for the PEC etching

To demonstrate the importance of sharp pits, deep PEC etchings were tested starting with both KOH-etched V-shape and DRIE-etched U-shape grooves, as shown in Fig. 2. Because the sharp tips in the V-grooves (Fig. 2(a-1)) induce a higher electrical field and attract the photo-generated electron holes (h⁺) more effectively, they get etched more than the surroundings and start dominating the etching. If the initial grooves were close enough to each other, the space charge regions (SCR) of adjacent walls overlap, i.e., the silicon between the trenches becomes depleted of electron holes, leaving the sidewalls intact as the trenches get deepened. As a result, HAR trenches with excellent sidewalls can be fabricated, as shown in Fig. 2(a-2). In the U-grooves of Fig. 2(b-1), on the other hand, the electric field is distributed on the bottom surfaces. Since the electric field is somewhat higher at the two corners, etching branches out and forms two independent trenches from one groove. Having started with less distinctive field concentrations, these branched-out trenches are less stable and form irregular sidewalls, as shown in Fig. 2(b-2). Although some reported successful PEC etching without sharp pits, the possible sizes of pits and pitches and applicable current density were severely limited. For example, Ohji [15] reported a PEC etching using initial pits made by isotropic wet etching and RIE, but only pore structure was studied. We have first confirmed that for a square array of pores the initial pits need not be sharp; etching morphology could be controlled mostly by the current density. For complex patterns, however, we could not obtain any good results.

Figure 3 shows the PEC etching with three different current densities, starting with DRIE-etched initial pits. The pattern is complex, consisting of a square array of pores and a meandering pattern of grooves. With a low current density, shown in Fig. 3(a), four independent pores formed under each square pit (made from a square opening in the photomask), and some randomly located pores formed under the meandering grooves, indicating the current density was too small. With an increased current density, shown in Fig. 3(b), one single pore with a larger diameter formed under each square pit, and denser pores formed under the meandering grooves. However, the current density cannot continue to be increased, as other limitations soon arise, such as the minimum distance between two adjacent trenches and stability of pore growth. Figure 3(c) shows the result when the current density

was increased further. Although the upper part of the etched trenches indeed achieved smooth sidewalls, the lower part was obviously over etched, indicating the current density became too high and unstable as the aspect ratio of the trenches grew high. Therefore, for the PEC etching to accommodate complex patterns, especially for HAR and VHAR structures, sharp pits are highly desired.

B. Surfactant-added TMAH etching

As described in the previous section, the Triton-added TMAH etching produced various patterns of V-grooves. Figure 4 shows the fabrication of V-grooves in a square-spiral and a zigzag pattern. Figures 4(a-1) and 4(b-1) show the PECVD SiO₂ patterns with a ~4 µm line width and spacing, which serve as the etching masks against the subsequent silicon pits etching. Figures 4(a-2) and 4(b-2) show the V-grooves etched in a solution of TMAH and Triton X-100. Notably, the addition of a small amount of surfactant in TMAH significantly reduced the undercut at convex corners and non-<110> edges while maintaining the bottom of the grooves nearly as sharply as the usual wet anisotropic etchings, such as KOH and TMAH, would generate. However, we have found a few important details to fabricate the V-grooves necessary for the deep PEC etching, as described below. The native oxide must be removed by HF prior to the surfactant-added TMAH etching so that the hydrophobicity of silicon surface promotes the adsorption of the surfactant layer [21]. During the surfactant-added TMAH etching, the etching time had to be precisely controlled. This is because once the V-grooves were formed and bounded mostly by {111} planes, the reactants started to lose the desired attributes: attacking convex corners, rounding concave corners, and undercutting the edges not aligned to <110> directions. While the patterns in [16]–[18] were several tens of microns in line widths, the patterns in our application have line width and spacing of only $\sim 4 \mu m$, demanding significantly more precise etching control. Another noteworthy issue is that mechanical agitation (e.g., magnetic bead stirring) during etching should be avoided [20], as the shear flows on the sample surface result in large fluctuations in the adsorbed surfactant thickness, which is considered a disadvantage in terms of repeatability and surface roughness [22]. Figures 4(a-3) and 4(b-3) show unacceptable V-grooves (note the undercuts) because of the excessive etching (>30 min).

C. Photo-electrochemical etching of silicon structures

Once the V-grooves are formed, PEC etching should be performed, for which two main etching parameters, i.e., the HF concentration and current density, should be optimized. While PEC etching of arrays of pores have been widely studied, often leading to aspect ratios over 100:1 [9]-[11], arrays of line patterns have been obtained only recently [23]-[25]. In a recent study [12], we have reported that deep pores can be formed from pits with a current density J much lower than the critical current density J_{ps} , which is exclusively dependent on the electrolyte concentration C_{HF} [26], e.g., $J = 2 \text{ mA/cm}^2$ and $J_{ps} \approx 43 \text{ mA/cm}^2$ for a 5 wt% HF. We have also reported that under the same condition, i.e., current density much lower than the critical current density, many discrete pores were formed along grooves rather than continuous trenches. To form a continuous trench, those discrete pores must be dense enough to merge, as illustrated in Figs. 2(a-1s) and 2(b-1s), which would require a higher current density. The PEC etching of complex patterns is similar to that of straight line patterns, but has a tighter window for successful processing, requiring more careful selection of C_{HF} and J. We first used a 2.5 wt% HF ($J_{ps} \approx 15$ mA/cm²) and a ratio of J/J_{vs} between 0.4 and 0.5. Figures 5(a-1) and 5(b-1) show the ~200 µm-tall square-spiral plates and 150 µm-tall zigzag plates formed after 5 and 3 hours of etching, respectively. Although it may seem that the trenches can be etched even deeper by simply increasing the etching time, further exploration revealed that the trenches tend to degenerate eventually in the 2.5 wt% HF. Figures 5(a-2) and 5(b-2) show the situation degenerated trenches after etching $\sim 300 \,\mu m$ deep for 9-10 hours. A possible reason for the degeneration is the decrease of electrolyte concentration deep at the bottom of the narrow trenches [27]. To reduce the effect of the F depletion, a higher concentration electrolyte may be considered. This consideration follows logic because the ratio between the reduced and the overall concentration becomes smaller if the starting concentration is higher. Besides, a higher concentration renders a higher etching rate. Therefore, we then used a 4 wt% HF ($J_{ps} \approx 30$ mA/cm²) and kept the ratio of J/J_{ps} at 0.4. Figure 6 shows the 300 µm-deep silicon structures after etching for ~5 hours. The initial patterns of pits (Figures 4(a-2) and 4(b-2)) have been successfully transferred in a highly anisotropic way. Uniformity and stability were excellent, as no apparent branching and over etching were observed over the entire processing area (0.5 cm²) during the etching. To our knowledge, this is the highest aspect ratio of complex patterns generated by PEC etching.

Compared with deep etching of pores in arrays and trenches in straight lines, the deep etching of complex patterns is significantly more difficult. Although optimized electrolyte concentration and current density can alleviate the degeneration, J_{ps} changes appreciably as the trenches grow deep. Moreover, the complex patterns make the electric field at the etching front much more complicated and difficult to predict. Therefore, if even deeper etching is desired, we suggest new provisions be developed to adjust the current density and refresh the electrolyte during the course of a long etching.

D. Freestanding micro metal structures

Usually, molding-based metal microstructures are fabricated by filling the voids in a pre-defined mold with a bottom-up electroplating. An issue is the gas trapped in the voids, which would make the resulting metal porous or even block the growth of the metal. Most known electroplating processes use a small amount of surfactant to help remove the gas bubbles in the voids. This simple remedy works well for a relatively low aspect ratio and even HAR voids, but it is unfortunately not sufficient for VHAR (e.g., over 100:1) voids. Vacuum degassing has been found to overcome this problem [12]. Vacuum degassing during electroplating can be found even in a decades-old patent [28], which stated that the air space above the electroplating bath was substantially evacuated and maintained at a pressure lower than atmospheric pressure during the electroplating. Because of the severe evaporation due to the vacuum bath, the technique required a complex apparatus to maintain the electrolyte concentration and bath temperature. A smooth and pit-free surface has been reported on flat surfaces. However, the technique was applied to electroplate on flat surfaces rather than filling mold structures. It is important to note that in order to fill VHAR voids this simple vacuum-plating method [28] hurts rather than helps, because the vacuum makes even a small amount of gas grow to form bubbles and block the voids. In a more recent patent [29], vacuum and venting were repeated several times before electroplating started, making the initially trapped bubbles drawn out from the cavities and dislodged from the mold surface. However, it has been difficult to reduce the accumulation of H_2 after the plating process started. The solution turned out surprisingly simple yet

effective: an intermittent degassing mechanism [12]. To remove the trapped air during the initial wetting of the mold, the pressure was lowered before electroplating started. Once the electroplating started, on the other hand, the bath was evacuated and vented hourly to prevent the hydrogen from being accumulated.

To fill the 4 μ m-wide and 300 μ m-deep trenches in the silicon molds shown in Figure 6, we needed to use the above electroplating technique [12]. After ~8 hours of nickel electroplating using 20 mA/cm² at a temperature of 40°C, the PEC-etched VHAR silicon molds (Fig. 6) were completely filled without any defect (Figs. 7(a-1) and 7(b-1)). To obtain freestanding micro metal structures, the silicon molds were removed by a XeF₂ etching at a pressure of 3000 mTorr for ~1 hour. Figures 7(a-2) and 7(b-2) show the final micro metal structures in a square-spiral and a zigzag pattern with an aspect ratio and height up to 60:1 and 250 μ m, respectively. The good uniformity and mechanical stability of the freestanding metal structures further proves the efficacy of the intermittent vacuum degassing-assisted electroplating technique [12].

E. Utilities of VHAR micro metal structures in complex patterns

Although we do not report any particular application here, the VHAR micro metal structures are of central interest for many applications, such as micro gas sensors [3], optical waveguides [4], 3-D micro batteries [5], and micro cooling devices [6], most of which take advantage of the large surface-to-volume ratio. Aside from the utilities of complex patterns for specific applications, here we point to a basic mechanical advantage of VHAR structures in complex patterns over the existing post and grating structures: structural stability. Note that as the slender structures become taller, i.e., HAR \rightarrow VHAR, the rigidity of the structures quickly decreases, causing adhesion between the structures, i.e., a classic stiction problem in MEMS. Not limited to the crystal direction anymore with the new technique reported here, one can increase the structural rigidity of the VHAR plates greatly by modifying the straight pattern of the plates into a slightly zigzagged pattern.

IV. SUMMARY

Employing the surfactant-added TMAH etching, which can generate sharp-pit grooves in complex patterns, and

optimizing the deep PEC etching process originating from the complex patterns, we have obtained VHAR trenches in complex patterns into silicon. Deep trenches of square-spiral and zigzag patterns (width = 4 μ m; space = 4 μ m; depth = 300 μ m) have first been prepared. Using this VHAR silicon as a mold and employing the vacuum-degassing-assisted electroplating, we further obtained a dense array of freestanding VHAR (up to 60:1) micro metal structures of complex patterns. Consequently, the restriction of the pattern direction in fabricating VHAR silicon and metal structures has been eliminated, which expands the versatility of PEC etching for silicon micromachining. Compared with the existing grating structures in an array of parallel straight lines, the structures of complex, e.g., zigzag, patterns can be made significantly more robust – important to obtain VHAR structures that are freestanding.

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Table I Comparison of the fabrication methods for high-aspect-ratio silicon microstructures

	DRIE	PEC etching		
References	[7], [8]	[9]-[11]	Recent [12]	This report
Max. aspect ratio	40:1	100:1	120:1	80:1
Pattern shape	Arbitrary patterns	Regular array of dots	Regular array of dots or straight lines	Complex patterns
Sidewall profile	Nearly straight with scalloped surface	Straight with smooth surface		



Fig. 1. Overall process to fabricate the HAR or VHAR silicon or metal microstructures in a complex pattern, drawn schematically and not to the scale. (a) Formation of sharp pits on silicon by surfactant-added TMAH etching. (b) PEC etching of HAR or VHAR silicon structures. (c) Deposition of a seed layer and filling the trenches by vacuum-degassed electroplating. (d) Removing silicon mold by XeF₂ etching.



Fig. 2. The progress of PEC etching, starting with initial pits that are sharp (a) or not sharp (b). (a-1) and (b-1) SEM pictures of KOH-etched V-shaped pits and DRIE-etched U-shaped pits, respectively. (a-1s) and (b-1s) Schematic illustration of the nucleation sites formed along the pits. (a-2) and (b-2) SEM picture of the trenches subsequently formed by deep PEC etching. For the case of U-shaped pits of (b), each pit branches out to two trenches of irregular sidewalls.



Fig. 3. Unsuccessful PEC etching for deep trenches, starting with DRIE-etched pits. (a) Low current density. (b). Medium current density. (c) High current density.



Fig. 4. Fabrication of initial V-grooves in complex patterns by anisotropic silicon etching in a solution of TMAH added with Triton X-100. (a-1) and (b-1) PECVD SiO₂ patterns before the groove etching; (a-2) and (b-2) V-grooves with sharp tips are formed after etching; (a-3) and (b-3) If the etching is excessive, the pits in the grooves lose the sharpness needed for deep PEC etching.



Fig. 5. Deep PEC etching of silicon in 2.5 wt% HF, starting with the V-grooves in complex patterns. (a) Plates of a square-spiral pattern after etching for 5 hours (a-1) and 9 hours (a-2). (b) Plates of a zigzag pattern after etching for 3 hours (b-1) and 10 hours (b-2).



Fig. 6. Deep PEC etching of silicon in 4 wt% HF, starting with the V-grooves in complex patterns. (a) Plates of a square-spiral pattern after ~5 hours of etching. (b) Plates of a zigzag pattern after ~5 hours etching. The sidewalls are straight; they appear irregular because of the way the cross section was made (physical breakage) across the patterned silicon.





(b-1)



