VERY-HIGH-ASPECT-RATIO MICRO METAL STRUCTURES OF NON-STRAIGHT PATTERNS

Guangyi Sun^{1,2*}, Xin Zhao², and Chang-Jin "CJ" Kim¹

¹University of California, Los Angeles (UCLA), California, U.S.A.

²Nankai University, Tianjin, China

ABSTRACT

A fabrication of a periodic array of very-high-aspect-ratio (VHAR) freestanding micro metal structures of regular (non-straight) patterns is presented. By combining a recently reported surfactant-added TMAH process, which creates the sharp pits in non-straight line patterns on a silicon surface, with a recently developed high-yield fabrication of VHAR micro metal structures, which was enabled by the vacuum-assisted electroplating into the electrochemically etched VHAR silicon mold, a new family of metal structures, e.g., VHAR plates in a zigzag and a spiral-like pattern with an aspect ratio and height up to 60:1 and 250 μm , respectively, have been demonstrated for the first time.

INTRODUCTION

The fabrication of high-aspect-ratio (HAR) micro metal structures is of central interest for many applications of microelectromechanical systems (MEMS). For example, a dense array of HAR metal posts was fabricated to serve as the three dimensional (3-D) electrodes [1] for 3-D micro batteries, which produce more energy and power than what traditional two dimensional 2-D planar electrodes do on a given footprint area while sustaining high discharge rates [2]. Recently, a high yield fabrication of a dense array of very-high-aspect-ratio VHAR (higher than 10) metal posts of aspect ratio up to 85:1, freestanding 425 μm tall, has been achieved by using improved photo-electrochemical etching of silicon and vacuum degassing-assisted electroplating [3]. However, the reported fabrication technique for VHAR metal posts in [3] is limited to either square or straight-line patterns in $\langle 110 \rangle$ directions on a (100) silicon wafer. Any other patterns off $\langle 110 \rangle$ (especially convex corners) suffer from being undercut during the sharp-pit etching, which is needed to initiate the photo-electrochemical etching for silicon mold fabrication. This crystal-direction-dependent undercut has been considered universal with all $\{111\}$ -bounded wet anisotropic etching methods that use KOH or TMAH etchant. Although attempts have been made to overcome this restriction of pattern directions by creating the initial pits in an arbitrary pattern using an isotropic wet etchant (e.g., HNA) or reactive ion etching (RIE) [4, 5], the subsequent photo-electrochemical etching tended to result in branches due to the lack of sharp pits, limiting the aspect ratio far below (no report larger than 20:1) than what a photo-electrochemical etching can produce for square patterns (i.e., $> 100:1$).

In the meantime, a surfactant-added TMAH process [6, 7] has shown that the addition of small amounts of surfactant (e.g., Triton X-100 ($\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$, $n=9-10$)) in TMAH can significantly suppress the undercut in all non- $\langle 110 \rangle$ directions. Without the undercut, the modified anisotropic etchant can etch arbitrary patterns with a minimal distortion. More importantly for our interest in photo-electrochemical etching, the etched pits by this method are equally as sharp along any patterns.

We hereby propose to fabricate VHAR micro metal structures of non-straight patterns by combining the above two recently developed techniques. We will first define the initial sharp pits of arbitrary directions using the above-referenced surfactant-added TMAH solution [6, 7]. Starting from these sharp pits, we will then exercise the improved photo-electrochemical etching to produce a

VHAR silicon mold [3]. Finally, we will utilize the vacuum degassing-assisted electroplating technique [3], which produces defect-free metal fillings in VHAR trenches, to obtain VHAR micro metal structures with various shapes not bounded by silicon crystal directions.

In this paper, we present the processing steps and details for the sharp pits fabrication, photo-electrochemical etching of silicon mold, and electroplating of nickel. Although this report is not written for any specific application, an important interest of ours is fabricating high-performance electrodes for 3-D micro batteries.

FABRICATION

The overall fabrication process for HAR and VHAR metal structures of non- $\langle 110 \rangle$ orientation is schematically shown in Figure 1. Four principal steps are involved: sharp pits formation (Figure 1 (a)), photo-electrochemical etching of silicon (Figure 1 (b)), metal filling (Figure 1 (c)), and silicon removal by XeF_2 etching (Figure 1 (d)).

Figure 1: Fabrication procedure of VHAR micro metal structures of non-straight patterns.

The first step is to form the sharp pits on a silicon surface needed to start the subsequent photo-electrochemical etching. An N-type (100) silicon wafer with 40-60 $\Omega\cdot\text{cm}$ resistivity is used and 500 nm SiO_2 is deposited on the surface by a STS Plasma Enhanced Chemical Vapor Deposition (PECVD) system. An array of various patterns with $\sim 4\ \mu\text{m}$ line width and $\sim 4\ \mu\text{m}$ spacing is then transferred to the SiO_2 layer by photolithography and one 90 s dry etching by Ulvac NLD-570 glass etcher, followed by a ~ 20 s BOE wet etching, serving as the etching mask in TMAH. Following the recipe for a moderate etching rate to $\langle 100 \rangle$ and a minimal undercutting to non- $\langle 110 \rangle$ directions [6, 7], the silicon is then etched in 25 wt% TMAH in water (Sigma-Aldrich) with 0.1% v/v Triton X-100 surfactant (laboratory grade, Sigma-Aldrich) at 60 $^\circ\text{C}$ for 24 min to form the sharp pits, which will serve as the nucleation sites for the subsequent photo-electrochemical etching.

After removing the PECVD SiO_2 layer in buffered oxide etchant (BOE), the silicon is etched in 4 wt% hydrofluoric acid (HF) in DI water (21 ml of 49% HF in total volume of 300 ml) at room temperature with the backside near-infrared (870 nm wavelength) illumination using a high-power light source (Marubeni America Corporation). A few droplets of a wetting agent (Kodak Foto-Flo) are added to the electrolyte to help remove the hydrogen bubbles generated during the etching, which is very important for VHAR holes etching. The etching current density and bias voltage are independently kept constant at 12 mA/cm^2 and 3 V, respectively. Next, the holes are opened from the backside using deep reactive ion etching (DRIE), and 2000 Å thermal SiO_2 is grown to electrically isolate the silicon surface during the subsequent metallization and prevent the bulk silicon get electroplated.

Next, to seal the openings on the backside of silicon mold, a Ti/Ni (100 Å/ 1000 Å) seed layer is evaporated followed by $\sim 50\ \mu\text{m}$ nickel electroplating at 5 mA/cm^2 . This nickel layer then serves as the metal seed layer for the subsequent vacuum degassing-assisted nickel electroplating step to fill up the VHAR silicon mold. Commercially available solution (Technic, Inc.) is used for the nickel electroplating, and nickel sheet is used as the counter electrode. Eventually, the silicon mold is removed by XeF_2 etching, and the VHAR micro metal structures emerge.

EXPERIMENTAL RESULTS AND DISCUSSION

Surfactant-added TMAH etching

Using the Triton-added TMAH etching, we have successfully obtained various patterns of pits to initiate photo-electrochemical etching. Figure 2 shows a spiral-like pattern and a zigzag. Figures 2(a) and 2(b) show the PECVD SiO_2 patterns with $\sim 4\ \mu\text{m}$ line width on silicon surface. Figures 2(c) and 2(d) show the etched grooves (i.e., sharp pits) by using a solution of TMAH + Triton X-100. Figures 2(e) and 2(f) show the high magnification SEM images. Notably, addition of a small amount of surfactant in TMAH significantly reduced the undercutting at convex corners and non- $\langle 110 \rangle$ edges, while maintaining the bottom of the pits apparently as sharp as other wet anisotropic etchings (e.g., KOH) would generate.

Figure 2: Fabrication of initial sharp pits for photo-electrochemical etching by using a solution of TMAH + Triton X-100. (a) and (b) PECVD SiO_2 patterns before etching; (c) and (d) pits with sharp tips after etching; (e) and (f) close view of etched pits.

During the surfactant-added TMAH etching, the etching time has to be precisely controlled, as once the mask openings take the V-shape, which is bounded by $\{111\}$ planes, the reactants start to attack more prominently on sharp convex and rounded concave corners and on the straight edges along the non- $\langle 110 \rangle$ directions. Compared with the reported patterns with several tens of microns line widths [6, 7], the patterns in our application have line width and spacing of only $\sim 4\ \mu\text{m}$, demanding more precise etching control. Another noteworthy issue is that any agitation (e.g., magnetic stir or ultrasonic) during etching should be avoided, as the agitation strongly reduces the effect of surfactant.

Photo-electrochemical etching

To fabricate VHAR silicon mold using photo-electrochemical etching, we have optimized etching parameters, including HF concentration (4 wt%), current density (12 mA/cm^2), and anodic bias voltage (3 V), succeeding in transferring the patterns of the initial pits (Figures 2(c) and 2(d)) more than $250\ \mu\text{m}$ deep in a highly anisotropic way, as shown in Figure 3, after ~ 5 hours of etching. Uniformity and stability were excellent, as no apparent branching and self-stopping of pores were observed over the entire processing area ($0.5\ \text{cm}^2$) during the etching. To our knowledge, this is the highest aspect ratio of regular (i.e., not aligned to crystal directions) patterns generated by a photo-electrochemical etching.

Figure 3: Photo-electrochemically etched very-high-aspect-ratio silicon mold by using TMAH + Triton X-100 etched initial pits. The side walls are straight; they appear irregular because of the way the cross section was made (physical breakage) across the patterned silicon.

Vacuum degassing-assisted electroplating

To fill the 250 μm -deep and 4 μm -wide trenches in the silicon mold shown in Figure 3, we needed to use the newly developed intermittent vacuum degassing-assisted electroplating technique [3]. Filling such a VHAR holes by electroplating without a defect throughout the height was not possible before because of the gas bubbles generated during the electroplating.

Usually, molding-based metal microstructures are fabricated by filling the voids in the silicon with 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 method works well for relatively low aspect ratio and even HAR voids but unfortunately not for VHAR voids (e.g., 100:1). Vacuum degassing has been found to overcome the problem [3]. In [8], the air space above the electroplating bath was substantially evacuated and maintained at a pressure lower than atmospheric pressure during the electroplating. A smooth and pits-free surface has been reported on a flat surface with no holes. However, the evaporation of water was greatly accelerated due to the vacuum bath, which requires more complex feed-through control. More importantly, for electroplating of VHAR voids, this vacuum-plating method hurts rather than helps, as the vacuum makes even a small amount of gas grow to form bubbles and block the voids. In [9], on the other hand, vacuum and venting were repeated several times before electroplating started, causing the initially trapped bubbles to be drawn out from the cavities and to dislodge from the surface. However, the lack of an effective degassing technique during the electroplating has been keeping it difficult to reduce the accumulation of H_2 after the plating process started. The solution was surprisingly simple for us yet effective. Unlike all other vacuum electroplating techniques, our technique [3] uses an intermittent degassing mechanism, as schematically shown in Figure 4. To remove the trapped air during the initial wetting of the mold, the pressure was lowered before electroplating started. During the electroplating, on the other hand, the tank was evacuated and vented periodically (e.g., hourly) to remove the hydrogen being accumulated.

Figure 4: Schematic illustration of intermittent vacuum degassed electroplating [3].

Using the new plating technique described above, a high quality metal filling in VHAR voids in the silicon mold has been achieved. After ~ 8 hours of nickel electroplating using 20 mA/cm^2 at a temperature of 40°C, the photo-electrochemically etched VHAR silicon molds (Figure 3) were completely filled without any defect (Figure 5).

Figure 5: Very-high-aspect-ratio nickel filling inside silicon mold with vacuum degassing-assisted electroplating.

Freestanding micro metal structures

To obtain the freestanding micro metal structures, the silicon molds were removed by a XeF_2 etching at a pressure of 3000 mTorr for ~ 1 hour. Figure 6 shows the final micro metal structures in a spiral-like and a zigzag pattern with an aspect ratio and height up to 60:1 and 250 μm , respectively. The good uniformity and mechanical stability of electroplated structures further proves the efficacy of the intermittent vacuum degassing-assisted electroplating technique [3].

Figure 6: Very-high-aspect-ratio micro metal structures released after XeF_2 etching.

CONCLUSIONS

By combining surfactant-added TMAH etching, which generates sharp pits in non-straight line patterns, with improved photo-electrochemical etching and vacuum-degassing-assisted electroplating, a dense array of VHAR (up to 60:1) freestanding micro metal structures of regular patterns (e.g. zigzag and spiral-like pattern) has been achieved. Consequently, the restriction of pattern directions in fabricating VHAR micro metal structures has been eliminated, which would expand the versatility of photo-electrochemical etching for micromachining. For our immediate application of 3D microbatteries, we will study the pattern design, the uniformity of photo-electrochemically etched trenches over a relatively large processing area (e.g., over 2 cm by 2 cm), and mechanical stability of the metal structures.

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CONTACT

*G. Sun, tel: +1-310-825-3977; guangyi@ucla.edu