Supporting Information

Uniform Vertical Trench Etching on Silicon with High Aspect Ratio by Metal-assisted Chemical Etching Using Nanoporous Catalysts

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1. Methods

Boron-doped (100) and (111)-oriented silicon wafers with (University Wafer, MA) with a resistivity of 1–10 Ω·cm were cleaned in Piranha solution (1:3 volume ratio H$_2$O$_2$:H$_2$SO$_4$) at 120 °C for 10 min, and then dipped in 1% w/w aqueous HF solution to remove the oxide layer. The (100)-type silicon substrates were used for most of the test unless specified. For electron beam lithography, a 350 nm-thick poly (methyl methacrylate) (PMMA A6, Microchem, MA) resist film was spun cast on silicon wafer and exposed in a JEOL-9300FS EBL system with a base dose of 400 μC/cm$^2$. The exposed wafer was developed in the mixture of isopropanol and methyl isobutyl ketone with a volume ratio of 1:1 for 2 min. For photolithography, a 1.6 μm-thick layer of positive resist Microposit S1813 (Shipley) was spun cast on the wafer and exposed in a mask aligner (Karl Suss MA6) by 405 nm UV light. The exposed wafer was developed in Microposit MF 319 developer. All the wafers with patterned resist are treated with oxygen plasma (RF power: 22 W) in a RIE tool (Plasma Therm Inc.) to remove any polymer residue on exposed areas and render the silicon surface as oxygen-terminated (Si-O); the Si-O surface can be altered as hydrogen terminated (Si-H) by immersing the Si-O sample in a buffer oxide etch (6:1) solution for 1 min and rinsing with copious deionized water. Water contact angle measurements were performed with a Rame-Hart goniometer with a charge-coupled device camera equipped for image capture. Au catalysts were deposited by an electron beam evaporator at a rate of 0.5 Å/sec in a vacuum atmosphere of 3×10$^{-6}$ Torr (CVC Product Inc.). In this report, the thickness refers to the nominal value measured by an in-situ monitor (Maxtek Sensor Crystal Gold 6MHz 74016-1139 P/N 103220, Inficon) unless specified.

To prepare the etchant, HF (48-52%wt in H$_2$O) and H$_2$O$_2$ (30%wt in H$_2$O, Anachemia Chemicals, LLC) were directly mixed without further processing. Deionzed water (DI water) was produced by a Thermo Scientific Barnstead Smart2Pure water purification system. The total volume of the etchant was fixed as 42 mL. The etching was conducted by gently immersed the sample in the etchant solution in a closed non-transparent polyethylene container for a certain amount of time at room temperature. No additional agitation was used. To fill the trench, an epoxy precursor (17g EPON Resin 862, Hexion Special Chemicals Inc.; 20 g Lindride 52D, Lindau Chemicals; one drop of imidazole catalyst, Shikoku) is cast on the etched sample and cured at 150 °C in an atmospheric oven for 1 hr. The polymer replica is isolated by completely removal of silicon in the mixture of HNO$_3$ (70%wt), HF (49%wt) and H$_2$O with the volume ratio of 1:1:1 overnight. Scanning electron microscope images were taken from Zeiss LEO 1530 thermally assisted field emission (TFE) SEM operating at 10 keV with a working distance between 2 and 7 mm with inserted Oxford EDS system. Atomic force microscope data was collected by Veeco Dimension Edge AFM with Bruker TESP-SS silicon tips (nominal tip radius: 2 nm). The Matlab7.0 software was used for modeling of hole concentration.

2. Hole concentration distribution modeling

The $D$ value is experimentally defined as

$$\sqrt{D t} = l_d = \sqrt{(d_{max} - d_b)^2 + ((w_o - w_b)/2)^2}$$

where the $l_d$ represents the nominal diffusion length, and $d_{max}$, $d_b$, $w_o$ and $w_b$ are defined in Figure 3(g). The parameters are measured from Figure 6(d) and their values are listed in Table S 1.
Table S1 Parameters for $D$ calculation

<table>
<thead>
<tr>
<th>Etchant</th>
<th>$(d_{\text{max}} - d_b)/\mu m$</th>
<th>$((w_o - w_b)/2)/\mu m$</th>
<th>$l_d/\mu m$</th>
<th>$D/m^2\text{ sec}$</th>
</tr>
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<tbody>
<tr>
<td>$\rho(0.18)^{189}$</td>
<td>0.2</td>
<td>4</td>
<td>4</td>
<td>$2.70 \times 10^{-13}$</td>
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</table>

3. Supplementary images

Figure S1 Cross-sectional SEM image of SiO-10 nm Au catalyst on silicon substrate viewed at $5^\circ$ tilting angle. Black arrows indicate nanopores in SiO-10 nm Au for possible through-catalyst mass transport.

Figure S2 (a) 2 μm-wide SiO-10 nm Au catalyst patterned by photolithography; (b) single trench etched by the catalyst shown in (a) in $\rho(0.37)^{18}$ etchant for 10 min.
Figure S3 (a) Top view and (b) cross-sectional SEM image of a trench etched by 2 μm-wide SiO-10nm Ag catalyst in ρ(0.37)^1.8 for 10 min. Inset of (a) shows an enlarged view of the bottom surface of the trench.

Figure S4 (a) Top view SEM of a 2 μm-wide SiO-5 nm catalyst. (b) Cross-sectional SEM images of a trench etched by the Au stripe in (a) in ρ(0.37)^1.8 for 10 min.
Figure S5 (a) Cross-sectional SEM image of a trench etched by 50 paralleled 2 μm-wide SiO-10nm Au catalyst with 2 μm spacing in ρ(0.37)1.8 for 10 min at 75 °C. (b) shows an enlarged view of one wall between two adjacent trenches.