

Supporting Information for

Metal-Catalyzed Electroless Etching of Silicon in Aerated HF/H₂O Vapor for Facile Fabrication of Silicon Nanostructures

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Silicon Nanowires Fabrication and Characterization: All chemicals used were purchased from Sigma–Aldrich. p-type 1-10 $\Omega \cdot \text{cm}$ Si(100) and n-type 2-3 $\Omega \cdot \text{cm}$ Si(100) wafers purchased from General Research Institute for NonFerrous Metals (GRINM) was cut into pieces and ultrasonically degreased in acetone and ethanol for 5-10 minutes. The Si pieces are cleaned in the boiling solution of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ for 20-40 minutes. After each cleaning step, the Si pieces were thoroughly rinsed with deionized (DI) water. The Si pieces were coated with Ag particle film in aqueous solution of 5% HF and 0.02 M AgNO_3 for 1 minute, and immediately rinsed with DI water and dried with nitrogen gas. Then the Si pieces were introduced into the reactor filled with atmospheric HF/ H_2O vapor for vapor phase etching at room temperature. The morphology of the samples was characterized using a high-resolution scanning electron microscope (Hitachi-4800) and a high-resolution transmission electron microscope (JEM 2100F) equipped with energy-dispersive X-ray spectrometer. The evolved hydrogen in the gaseous reaction products is characterized using a Gas Chromatography (GC) equipped with a thermal conduction detector and a 5A molecular sieve column ($\Phi 3 \times 3\text{m}$) with nitrogen serving as the carrier gas.

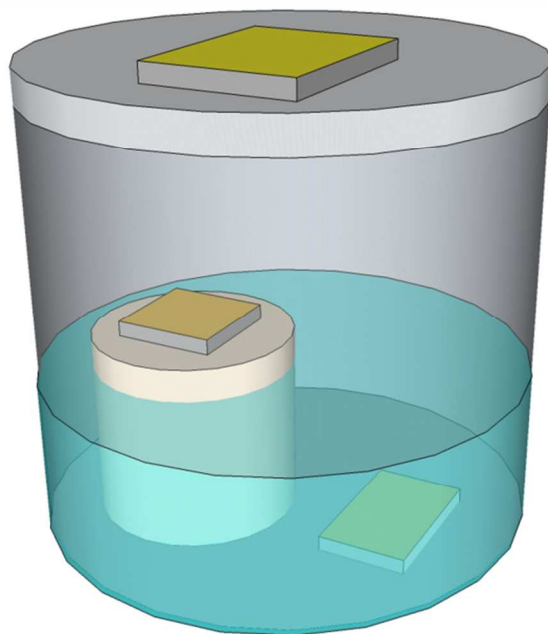


Figure S1. Schematic illustration of MACE of silicon in atmospheric HF/H₂O vapor. As a reference, two silicon substrates coated with AgNPs were placed in air outside the reactor (HF-free) or in aqueous HF solution, respectively.

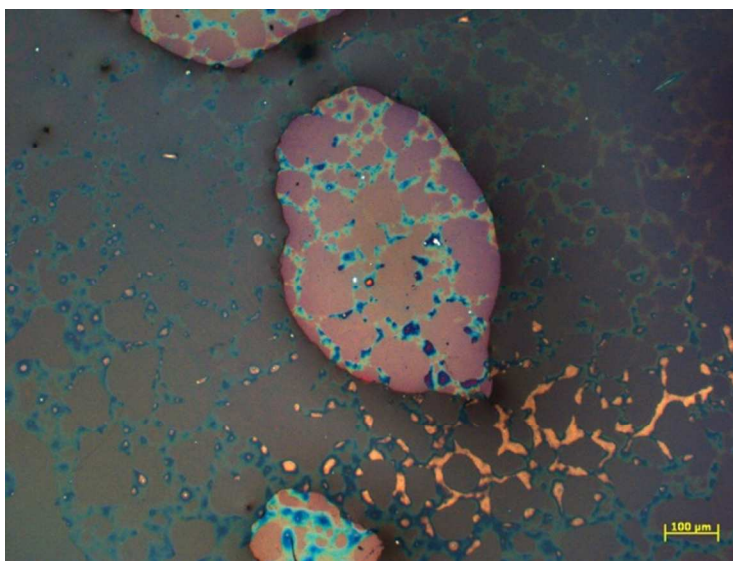


Figure S2. Microscope graph of the invisible electrolyte layer condensed on silicon surface after 15 minutes.

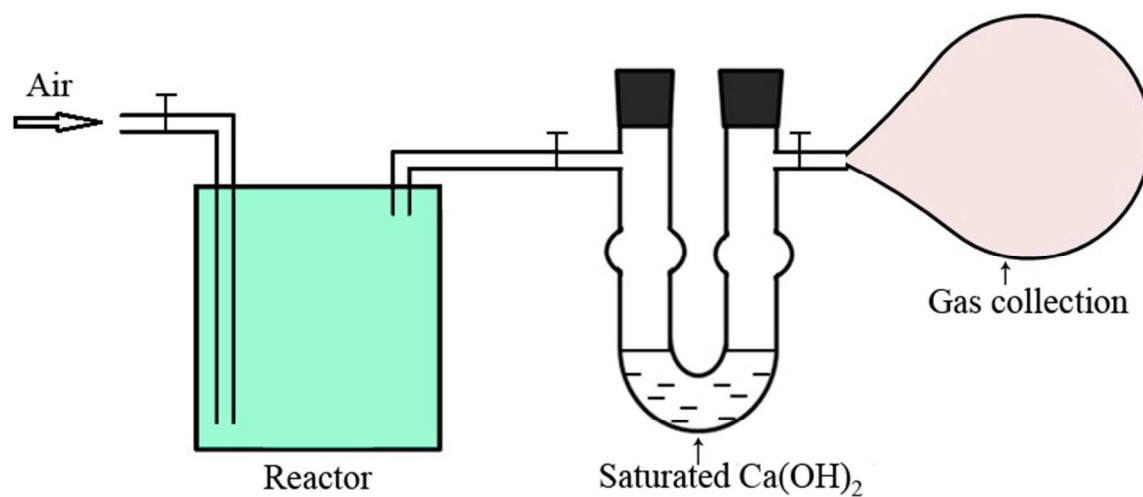


Figure S3. Schematic illustration of the experimental setup for gaseous product collection.

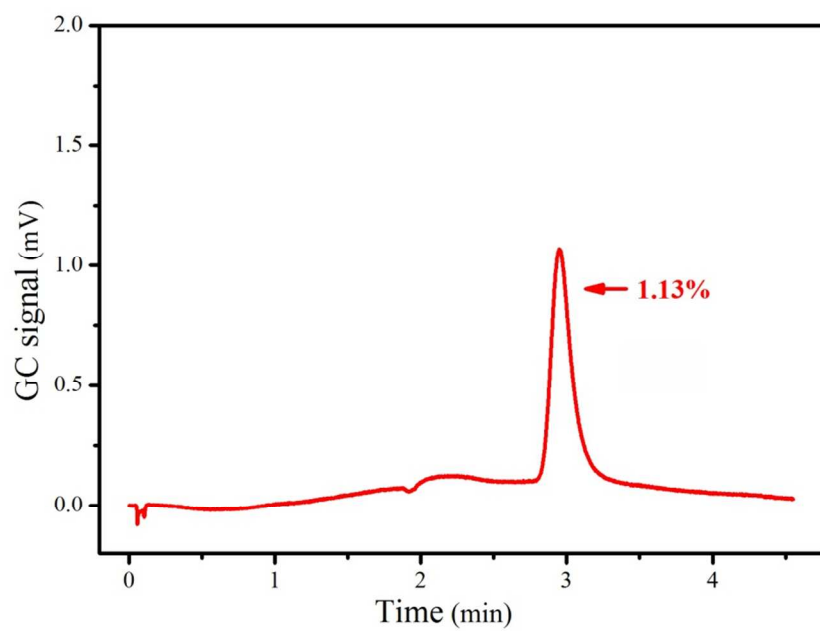


Figure S4. A typical gas chromatography (GC) trace of evolved hydrogen.

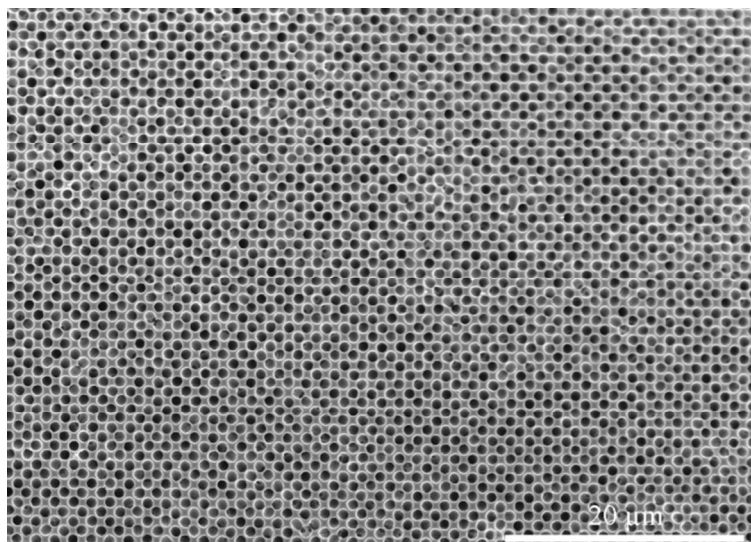


Figure S5. SEM image of ordered silicon nanohole array on p-type 1-10 $\Omega \cdot \text{cm}$ Si(100) substrate produced by the combination of deep ultraviolet lithography (UVL) and enhanced MCEEE of silicon in aerated HF/H₂O vapor.

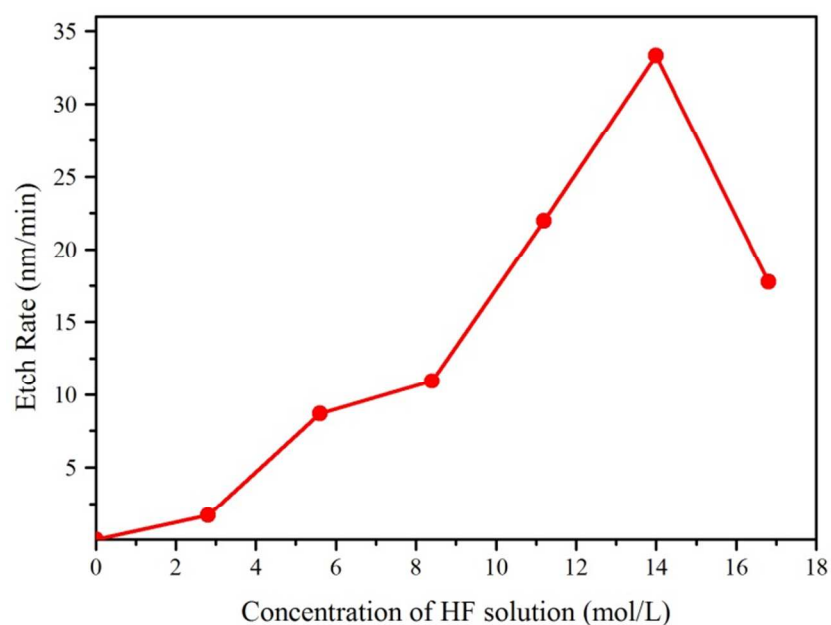


Figure S6. Plot of experimental etch rate of silicon against concentration of aqueous HF solution used for vaporization.

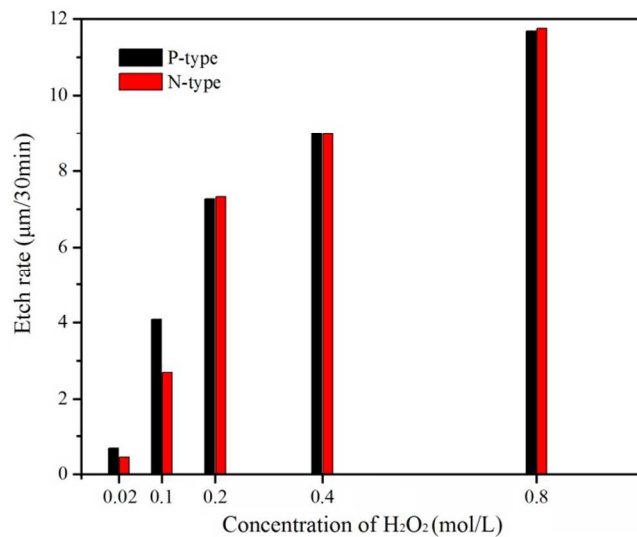


Figure S7. Comparison of etch rate of 1-10 $\Omega \cdot \text{cm}$ p-Si(100) and 2-3 $\Omega \cdot \text{cm}$ n-Si(100) by MCEE in aqueous HF- H_2O_2 solution.

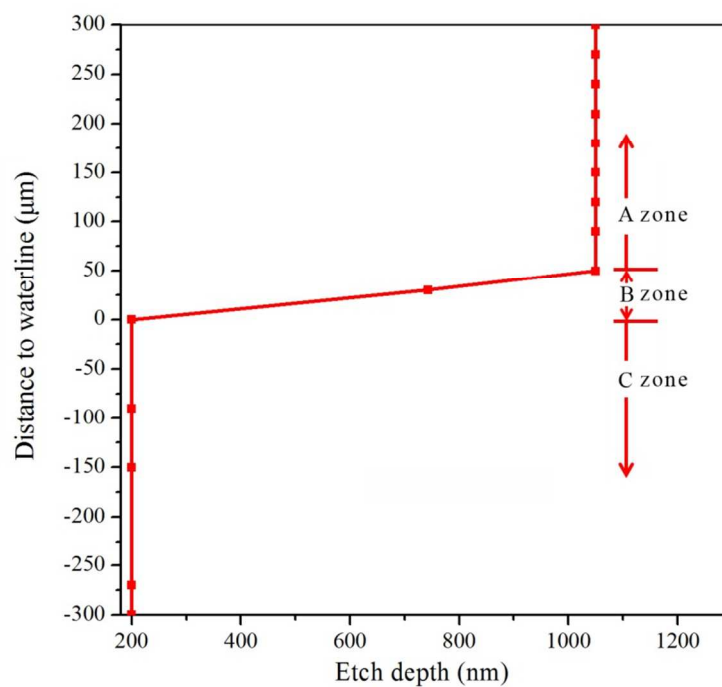


Figure S8. Plot of the silicon etch depth in 30 min vs. distance to waterline