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Electronic Supplementary Information for

Facile generation of surface structures having opposite tone in metal-assisted chemical etching of Si: pillars vs. holes

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Fig. S1 Etching evolution of Si by AgNO₃-based etching. (a to d) AgNO₃/HF/H₂O etching with PS colloidal monolayer mask, and (e to h) Ag nucleation with AgNO₃/HF/H₂O for 1 min. followed by H₂O₂/HF/H₂O etching. Scale bars are 1 μ m for all images, but 100nm for (e). Insets show large area view of the samples, and scale bars are 1 μ m for (a) and (e), and 10 μ m for (c) and (g), respectively.

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Fig. S2. Effect of deposited Ag thickness on the Si etching with H2O2/HF for 30min. For thin Ag films, thinner than ~30nm, no clear definition of pillar structure has been observed due to absence of connectedness or cohesion of Ag mesh film. As Ag thickness increases over 50nm, however, the clean pillar shape emerges. Note here that the uprightness of the Si pillars for thick Ag films improves as the thickness increases. At the same time, the pillar top becomes rough as the Ag film gets thicker. Considering these observations, the optimal thickness of Ag mesh seems to be 150~300nm.



Fig. S2 (continued).



Fig. S3 Morphology change of Ag(200nm) mesh film upon O_2 RIE treatment. (a) pristine Ag mesh film, and (b) after O_2 RIE treatment at 300W for 60sec. The Ag mesh film was severely damaged by RIE, which has led to easy delamination during MaCE, even at such lower thickness compared to critical thickness of ~600nm.

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Fig. S4 Improved surface roughness of Si structures by post-processing or bilayer metal mseh catalyst. (a) Si pillar arrays after dry thermal oxidation (1100° C, 1hr) and oxide strip by HF, and (b) Si hole arrays prepared by using bilayer of metal, Cr(100nm)/Ag(200nm). After O2 RIE treatment, the empty holes were filled with sputtered and re-deposited Ag. Then the following MaCE has led to Cr/Ag mesh film delamination, leading to hole arrays etching. The Cr/Ag bilayer mesh protect the un-etched Si surface until it completely delaminated off the surface, resulting in the improved surface roughness.