Supporting Information for

"Au/Ag Bi-Layered Metal Mesh as a Si Etching Catalyst for Controlled Fabrication of Si Nanowires"

J. Kim,[1,3] H. Han,[1] Y.H. Kim,[1] S.-H. Choi,[3] J.-C. Kim,[1] W. Lee[1,2*]

[1]*Korea Research Institute of Standards and Science, Yuseong, 305-340 Daejeon (Korea)*

[2]*University of Science and Technology (UST), Yuseong, 305-333 Daejeon (Korea)*

[3]*Department of Applied Physics, Kyung Hee University, Yongin 446-701 (Korea)*

e-mail: woolee@kriss.re.kr

Figure Captions for Supporting Information.

Figure S1. (a,b) SEM images of silver nanoparticles deposited on Si(100) wafer from aqueous mixture solution of 5M HF and 0.005 M $AgNO_3$ for 90 s at room temperature; (a) a low and (b) high magnification. (c,d) Top-view and (e-g) cross-sectional SEM images of the corresponding wafer etched in aqueous mixture solution of 8.602 M HF and 0.375 M H_2O_2 (ε = [HF]/[H_2O_2] = 22.939) for 1 h at room temperature. A magnified plane-view SEM image shown in (d) indicate that silicon nanostructures formed by chemical etching are characterized by wall-like morphology, rather than uniform wire-like morphology. A magnified cross-sectional SEM image displayed in (d) shows irregular and porous etched profiles at the upper part of the etched sample. Ag^+ ions shed by silver catalyst particle via oxidative dissolution are thought to play a key role for prosification of etched silicon nanostructures.[1-4] As shown in (g), on the other hand, silicon nanostructures near the etching front exhibit wire-like morphology and smooth etched profiles, although the size distribution of nanostructures appears to be broad.

Figure S2. SEM micrographs showing dissolution-induced structural failure of silver mesh during metal-assisted chemical etching of a silicon wafer: (a) SEM image of as-prepared 20 nm-thick silver mesh with arrays of nanoholes; (b) SEM image of (100)-oriented silicon wafer etched in aqueous mixture solution of 12.698 M HF and 0.554 M H_2O_2 (ε = [HF]/[H_2O_2] = 22.921) at room temperature.

Figure S3. SEM micrographs showing the morphologies of silicon nanostructures formed by metal-assisted chemical etching of Si(100) wafers at room temperature in (a) 2.051 M HF and 1.789 M H_2O_2 (ε = [HF]/[H_2O_2] = 1.146), (b) 8.511 M HF and 7.423 M H_2O_2 (ε = 1.147), (c) 4.444 M HF and 7.753 M H_2O_2 (ε = 0.573), and (d) 2.222 M HF and 7.753 M H_2O_2 (ε = 0.287). Under etchant conditions with ε < 0.3, Au/Ag bi-layered metal meshes were immediately peeled from the silicon surface upon immersing into the etching solution, leaving behind arrays of surface nanopatterns shown in (d). The phenomenon can be attributed to dominant formation of thick oxidized layer over removal of oxidized silicon at low HF and high H_2O_2 concentration, which are reminiscent of etchant conditions yielding polished silicon surfaces in Ag nanoparticle-based chemical etching of silicons.[5]

Table Caption for Supporting Information.

Table S1. Relation between surface bond orientations, atomic arrangements, surface atom density, the effective number of back bonds per a silicon, the effective number of back bonds per unit area for Si(100), Si(110), and Si(111) planes; a = lattice constant of cubic silicon.

References for Supporting Information.

(1) Qu, Y.; Liao, L.; Li, Y.; Zhang, H.; Huang, Y. *Nano Lett.* **2009**, *9*, 4539.

(2) Chiappini, C.; Liu, X.; Fakhoury, J. R.; Ferrari, M. *Adv. Funct. Mater.* **2010**, *20*, 2231.

(3) Lee, C.-L.; Tsujino, K.; Kanda, Y.; Ikeda, S.; Matsumura, M. *J. Mater. Chem.* **2008**, *18*, 1015.

(4) Hochbaum, A. I.; Gargas, D.; Hwang, Y. J.; Yang, P. *Nano Lett.* **2009**, *9*, 3550.

(5) Chartier, C.; Bastide, S.; Lévy-Clément, C. *Electrochim. Acta* **2008**, *53*, 5509.

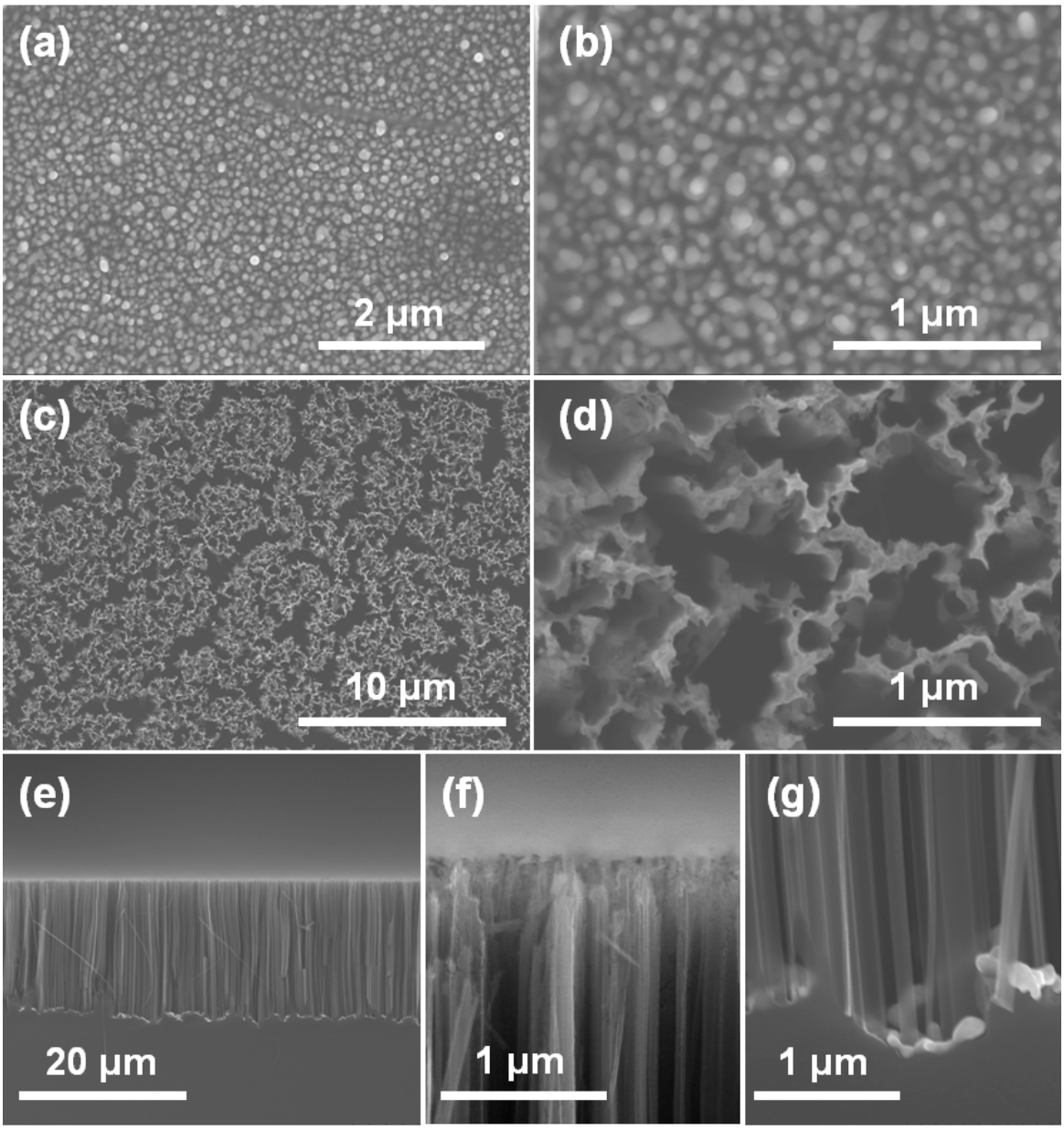


Figure S1. (a,b) SEM images of silver nanoparticles deposited on Si(100) wafer from aqueous mixture solution of 5M HF and 0.005 M $AgNO_3$ for 90 s at room temperature; (a) a low and (b) high magnification. (c,d) Top-view and (e-g) cross-sectional SEM images of the corresponding wafer etched in aqueous mixture solution of 8.602 M HF and 0.375 M H_2O_2 (ε = [HF]/[H_2O_2] = 22.939) for 1 h at room temperature. A magnified plane-view SEM image shown in (d) indicate that silicon nanostructures formed by chemical etching are characterized by wall-like morphology, rather than uniform wire-like morphology. A magnified cross-sectional SEM image displayed in (d) shows irregular and porous etched profiles at the upper part of the etched sample. Ag^+ ions shed by silver catalyst particle via oxidative dissolution are thought to play a key role for prosification of etched silicon nanostructures.[1-4] As shown in (g), on the other hand, silicon nanostructures near the etching front exhibit wire-like morphology and smooth etched profiles, although the size distribution of nanostructures appears to be broad.

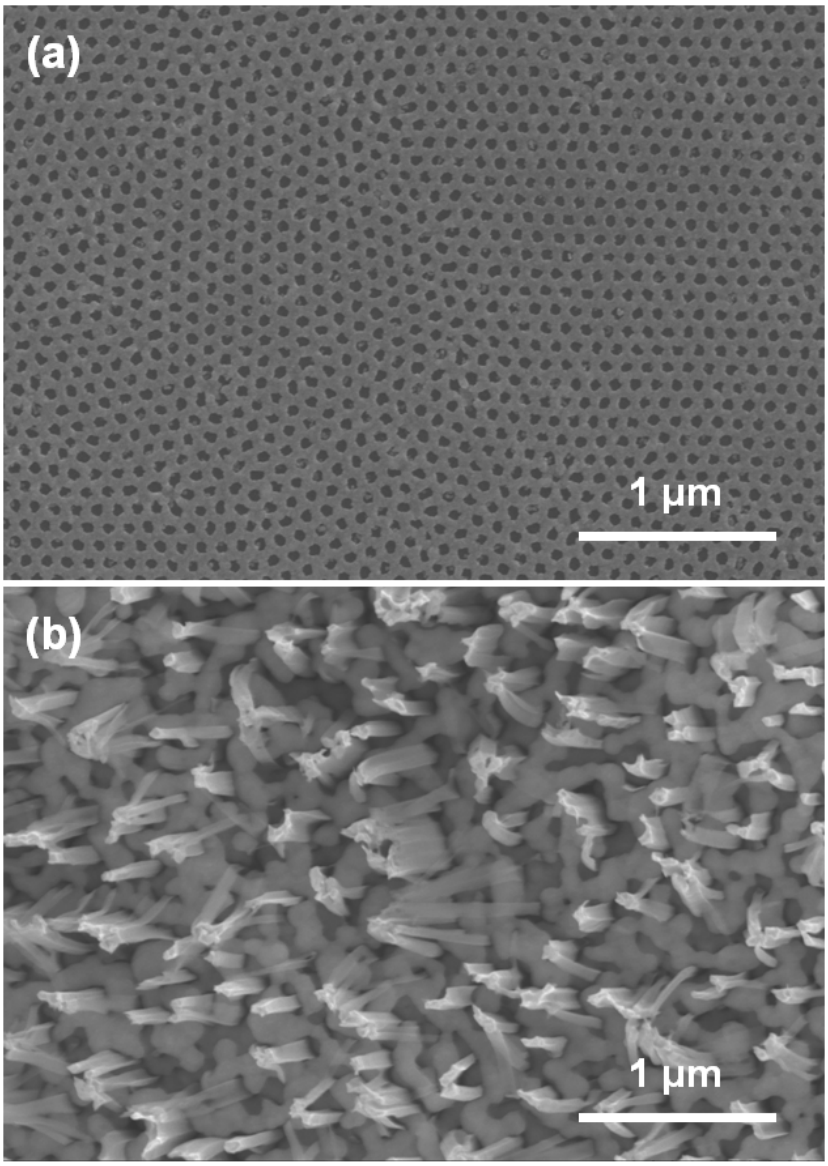


Figure S2. SEM micrographs showing dissolution-induced structural failure of silver mesh during metal-assisted chemical etching of a silicon wafer: (a) SEM image of as-prepared 20 nm-thick silver mesh with arrays of nanoholes; (b) SEM image of (100)-oriented silicon wafer etched in aqueous mixture solution of 12.698 M HF and 0.554 M H_2O_2 (ε = [HF]/[H_2O_2] = 22.921) at room temperature.

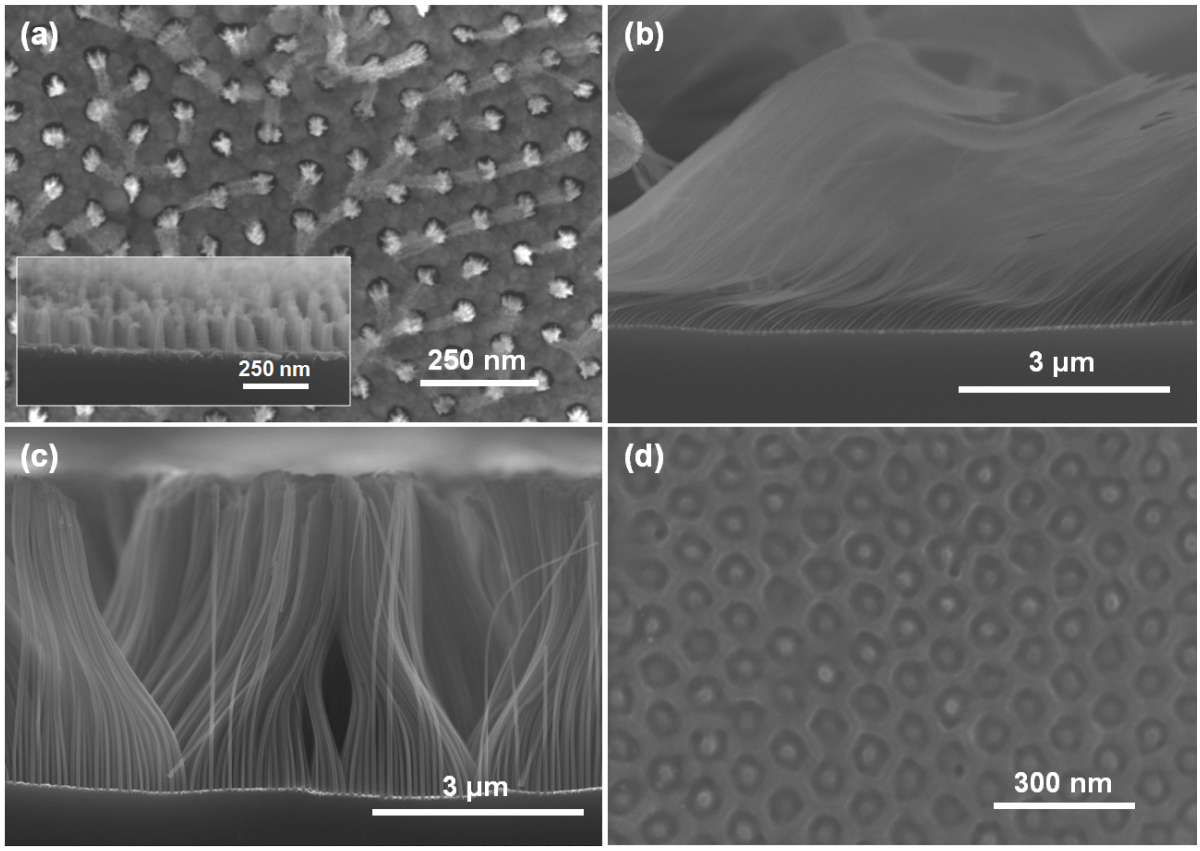
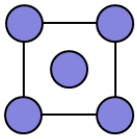
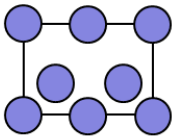
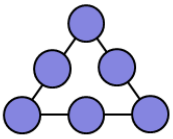
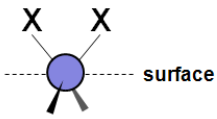
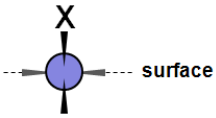
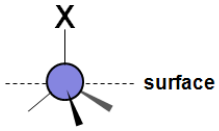


Figure S3. SEM micrographs showing the morphologies of silicon nanostructures formed by metal-assisted chemical etching of Si(100) wafers at room temperature in (a) 2.051 M HF and 1.789 M H_2O_2 (ε = [HF]/[H_2O_2] = 1.146), (b) 8.511 M HF and 7.423 M H_2O_2 (ε = 1.147), (c) 4.444 M HF and 7.753 M H_2O_2 (ε = 0.573), and (d) 2.222 M HF and 7.753 M H_2O_2 (ε = 0.287). Under etchant conditions with ε < 0.3, Au/Ag bi-layered metal meshes were immediately peeled from the silicon surface upon immersing into the etching solution, leaving behind arrays of surface nanopatterns similar to that shown in (d). The phenomenon can be attributed to dominant formation of thick oxidized layer over removal of oxidized silicon at low HF and high H_2O_2 concentration, which are reminiscent of etchant conditions yielding polished silicon surfaces in Ag nanoparticle-based chemical etching of silicons.[5]

Table S1. Relation between surface atomic arrangements, surface bond orientations, surface atom density, the effective number of back bonds per a silicon, the effective number of back bonds per unit area for Si(100), Si(110), and Si(111) planes; a = lattice constant of cubic silicon.

	(100)	(110)	(111)
Surface atom arrangement			
Interplanar distance (Å)	**5.43**	**3.84**	**2.35**
Surface atom density	$2/a^2$	$2.828/a^2$	$2.309/a^2$
Bond configuration			
Effective number of back bonds per a silicon atom	**1**	**2**	**3**
Effective number of Si back bonds per unit area (a^2)	**2**	**5.656**	**6.927**