

Supplementary Information

Morphological Transition of Si Surfaces from Solid Nanowires to Porous Nanobelts at Room Temperature

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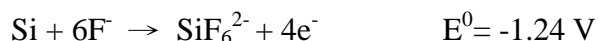
S1 Experimental details

Single-step MACE processes were performed on single-crystal Si wafers. Prior to the etching process, Si substrates were cleaned by rinsing with acetone, ethanol and DI water several times. The cleaned substrates were soaked in an aqueous solution containing 0.02 M AgNO₃ and 4.5 M HF at 25^oC. The involving electrochemical reactions are as follows:

Cathodic reaction:



Anodic reaction:



Overall reaction:



The electrochemical reaction started from the reduction of Ag ions to numerous Ag seeds covering the Si surfaces, Meanwhile, these formed Ag seeds oxidized the Si beneath at Ag/Si interfaces, and subsequently the oxidized Si atoms were dissolved to SiF₆²⁻ by HF enchants.

The morphologies and microstructures of as-fabricated Si nanostructures were characterized by scanning electron microscope (SEM, JSM-6390) and high resolution transmission electron microscope (HRTEM, JEOL 2010) investigations, respectively. The photoluminescence (PL) spectra of Si nanostructures were measured by the continuous-wave μ-PL system using a He-Cd laser (325 nm) as the excitation source

at room temperature.

The diffusivity of Ag^+ in catalytic etching of Si was estimated by the following equation¹,

$$D = AT/\eta^P$$

Where D represents the diffusion coefficient (cm^2S^{-1}), A an empirical constant, η the solvent viscosity (Pa's) and P the viscosity exponent and can be expressed by¹,

$$P = -1.296 / r + 1.666$$

where r is the radius of Ag ion².

S2 Morphological investigations of Si surfaces textured by water-based and EG-based MACE method

The formation mechanism of porous Si nanowires through MACE method can be contributed by two pathways^{3,4}: one emerges from the anisotropic dissolution of Si along [100] direction induced by the primary Ag nanoparticles, resulting in the solid nanowires afterward; the other necessitates the existence of secondary Ag nanoclusters, which are mainly converted from the primary Ag nanoparticles by H_2O_2 oxidant and re-nucleated on the sidewalls of nanowires, initiating the catalytic porosification of Si. Specifically, it has been reported that the dopant-induced defects in heavily doped Si wafers act as a crucial rule in initializing the re-nucleation of secondary Ag nanoclusters and are needed for the pore formation³⁻⁶. In contrast, to prepare the porous nanowires through Ag assisted etching on the lightly doped Si without using any additional oxidant, i.e., H_2O_2 , an alternative formation pathway must exist.

To unveil the influences of solvents on catalytic etching of Si, one-step MACE processes were performed with DI water and ethylene glycol (EG) as solvents, respectively. First, as shown in Fig. S1a, numerous Ag seeds in DI-water based electrolytes are formed during 15 sec-reaction by injecting holes to the valence band of silicon, owing to the fact that electrochemical potential of Ag^+/Ag is more positive than the Fermi level of Si. Subsequently, after 1 min-reaction these Ag seeds with high surface coverage ($\sim 10^{10} \text{ cm}^{-2}$) act as primary etching fronts, which initialize the directional dissolution of Si and are maintained by the reduction of more Ag^+ ions on them, as depicted in Fig. S1c. As the Ag precipitates were removed by dipping sample in concentrated HNO_3 (65%), a branch of Si nanowires can be clearly observed in Fig. S1e. Additionally, we performed the MACE process with the presence of EG as solvents. It can be found that the similar charge transfer takes place and thereby the primary Ag seeds are deposited on the top surfaces of Si [Fig. S1b]. Notice that in

comparison with water-based MACE process, the decreased surface coverage of Ag nanoparticles ($\sim 10^9 \text{ cm}^{-2}$) obtained from EG-based MACE process explicitly reveals the retarded kinetics of electrochemical reaction due to higher viscosity of EG involved electrolytes. These primary Ag nanoparticles with separated distribution sink into Si underneath while the dissolution of Si proceeds, leading to the formation of nanopillars with belt-like shape [Fig. S1d]. Meanwhile, numerous secondary Ag nanoclusters are also generated on the surfaces of remaining Si nanobelts, as marked in Fig. S1d, and one can clearly observe the resulting nanopores accompanied with nanobelt formation after dissolving all the Ag precipitates by HNO_3 acid [Fig. S1f]. In addition, the microstructures of as-prepared Si porous nanobelts were characterized by high resolution transmission electron microscope (HRTEM) investigations, as shown in Fig. S2.

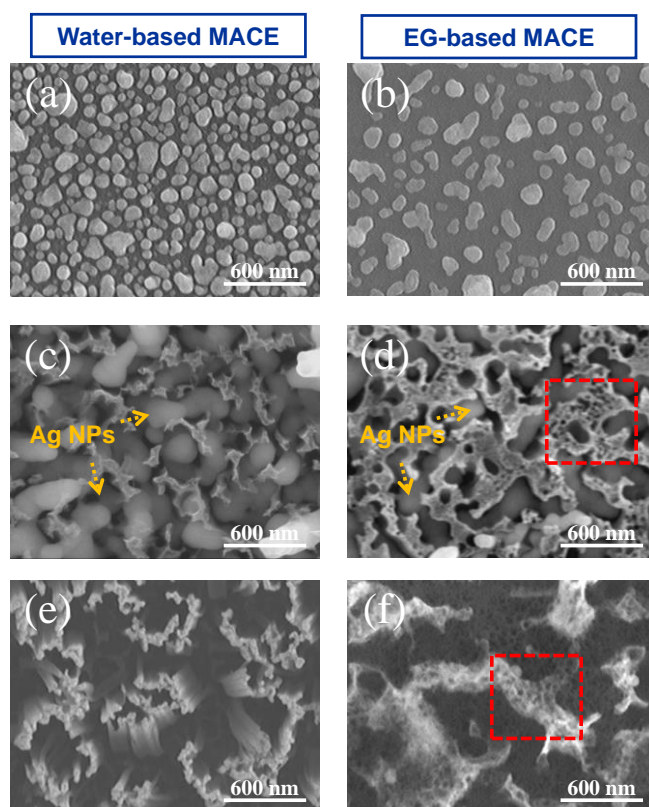


Fig. S1. Top-view SEM image of fabricated solid nanowire arrays via water-based MACE method for (a) 15-sec reaction, (c) 1-min reaction, (e) 1-min reaction and subsequent immersion in HNO_3 . Top-view SEM image of fabricated porous nanobelt arrays via EG-based MACE method for (b) 15-sec reaction (d) 1-min reaction, (f) 1-min reaction and subsequent immersion in HNO_3 . The red square in Fig. 1(d) and 1(f) evidences the formation of small pits on the top surface of nanobelts.

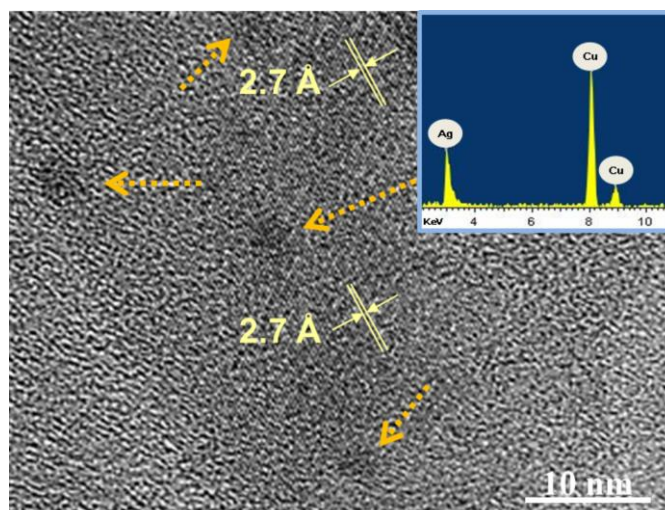


Fig. S2. HRTEM image of a porous Si nanobelt. The insert indicates the chemical composition of remaining Ag nanocluster on the nanobelt surface.

S3 Porous nanobelts prepared from Si substrates with various doping contents

Similar pre-clean treatment and one-step MACE processes were performed on three various Si (100) substrates, and the resulting morphologies were characterized by SEM observation, as shown in Fig. S3.

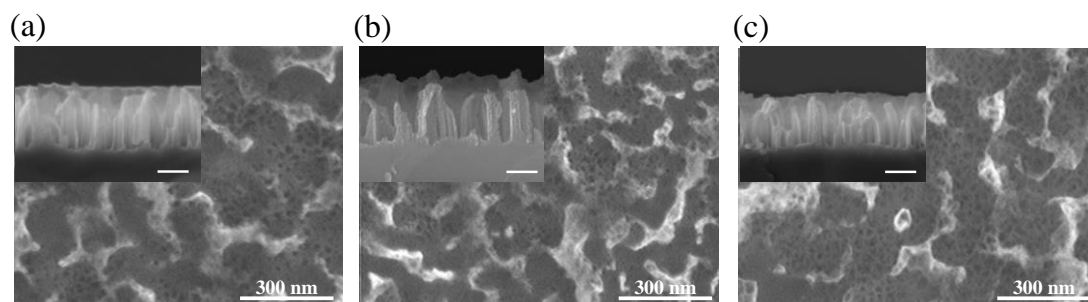


Fig. S3. Top-view SEM images of porous nanobelt arrays via EG-based MACE method from various types of Si substrates. (a) n type (0.01 to 0.05 Ωcm). (b) p type (0.01 to 0.05 Ωcm). (c) p type (0.001 to 0.005 Ωcm). The inserts show the corresponding SEM images in cross-sectional view, respectively. The scale bar in the inserts is 100 nm.

References

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