Supplementary Information

Room-temperature fabrication of three-dimensional porous silicon framework inspired by polymer foaming process

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Experimental Section:

Chemicals. Silver nitrate ($AgNO_3$), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), hexamethylenetetramine (HMTA), nitric acid (HNO_3, 65 %), sulphuric acid (H_2SO_4, 98 %), hydrogen fluoride (HF, 40 %), hydrogen peroxide (H_2O_2, 30 %), anhydrous methanol (MeOH), sodium hydroxide (NaOH) were supplied by Shanghai Chemical Reagent Company and used as received. N-doped Si (100) wafers (2 inches in diameter, 500 μm in thickness, 1-10 Ω·cm) and P-doped Si (100) wafers (2 inches in diameter, 2000 μm in thickness, 0.002-0.006 Ω·cm) were purchased from Zhejiang Lijing Photoelectric Science & Technology Company.

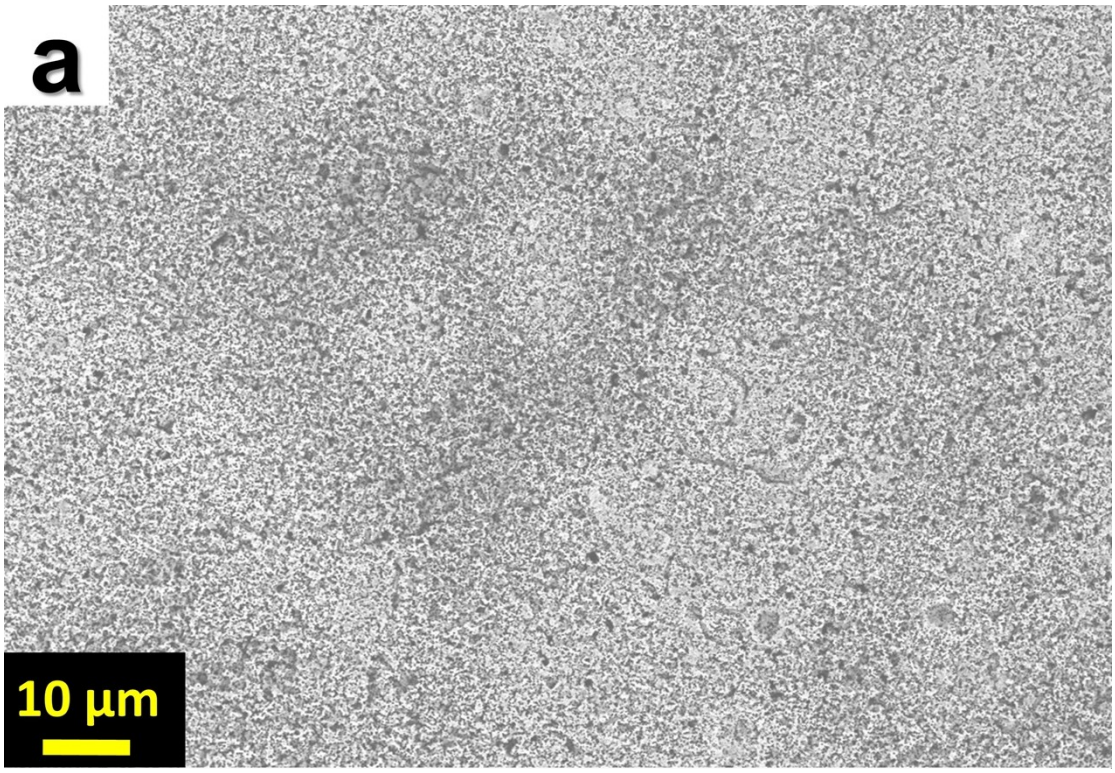
Two-step MACE treatment of Si wafer. All Si wafers were cleaned in piranha solution at 120 °C for 1 h followed by rinse with distilled water for 30 min, and then immersed into 5 % HF solution for 20 min to remove the oxide slayer. In a typical MACE run, a wafer was placed in 100 mL mixed solution of HF (4.8 M)/$AgNO_3$ (0.01 M) for 3 min in order to deposit Ag nanoparticles. After rinse with distilled water to remove the residual HF/$AgNO_3$ solution, the wafer was immediately put into 100 mL mixed solution of HF (4.8 M)/H_2O_2 (0.12 M). The etching was allowed to proceed at 25 °C for 18 h in the dark without stirring. Finally, the etched wafer was rinsed with distilled water, and immersed into 10 % HNO_3 for 20 min to remove residual Ag particles trapped inside.

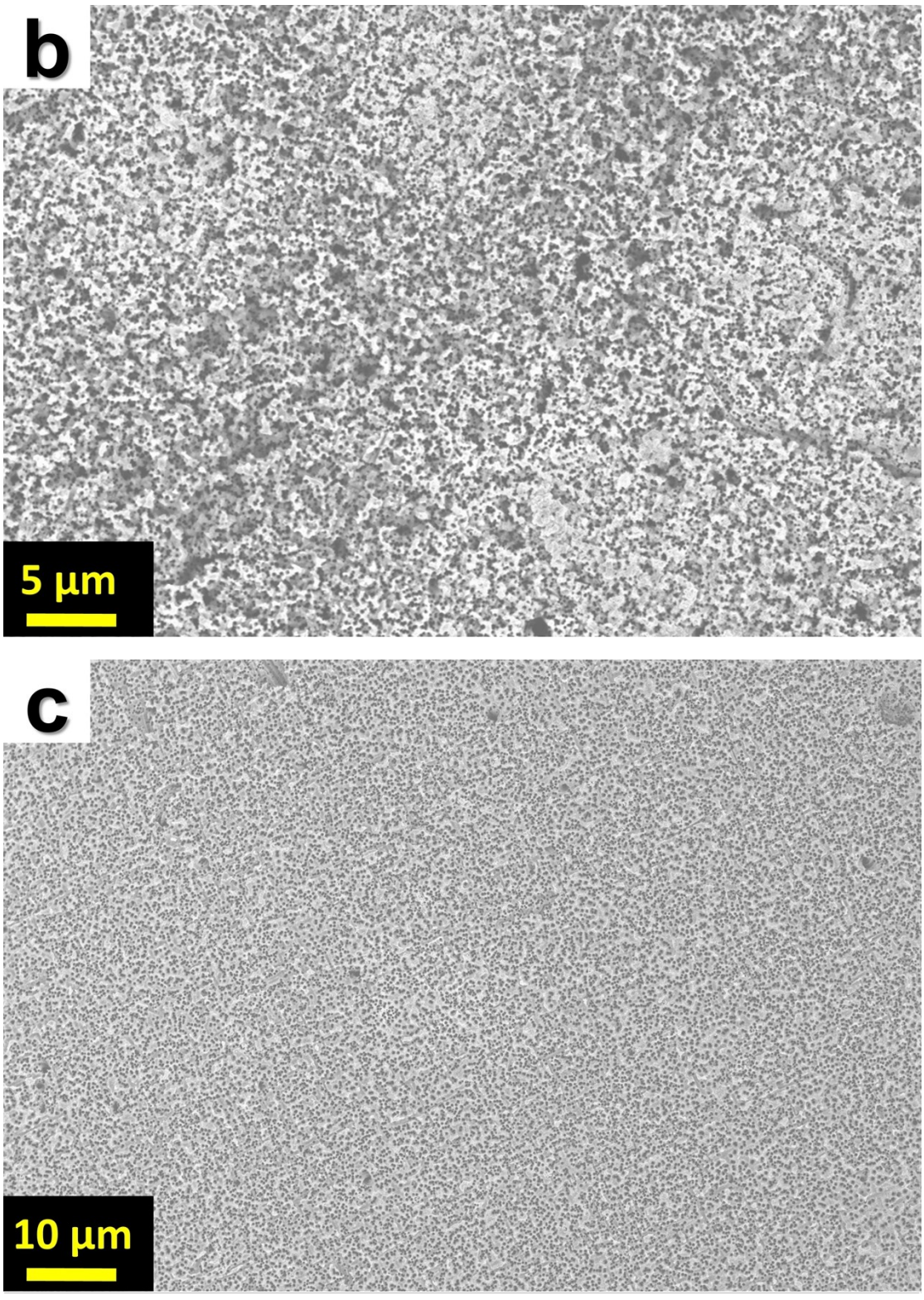
Preparation of 3D porous Si framework. The Si wafer previously treated by MACE was soaked in 30 % HNO_3 for 10 min in order to improve the hydrophilicity. After rinse with distilled water, the wafer was dried in vacuum at 90 °C for 2 h. For HF/HNO_3 etching, a mixture of 30 mL HF (40 %), 50 mL HNO_3(65 %) and 110 mL distilled water was prepared as etchant. The dried wafer was immersed in the etchant at 25 °C for 10 to 60 min depending on the targeted pore size. Note that the reaction is exothermic and the etching process is highly temperature sensitive.

So a good temperature control of the reaction media is recommended, especially for the etching of whole wafers. For HF/H_2O_2 etching, the etchant was comprised of 25 mL HF (40 %), 50 mL H_2O_2 (30 %) and 25 mL distilled water. The reaction proceeded in the same manner as HF/HNO_3 etching for 18 h.

Preparation of hierarchical porous composite framework of Si/ZnO. 25 ml solution of NaOH (0.12 g) in MeOH was added dropwise into 75 mL solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.219 g) in MeOH at 60 °C, and the mixture was stirred at 600 rpm for 3 h. The N-doped silicon wafer treated by MACE and 60 min HF/HNO_3 etching was dip-coated 4 times in the ZnO nanocrystal solution prepared above, and annealed at 150 °C for 10 min. Subsequent hydrothermal growth of ZnO nanowires was performed by immersing the wafer into 100 mL aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.744 g) and HTMA (0.35 g) at 90 °C for 3 h without stirring. Note that the wafer should be placed vertically to avoid undesired deposition from the solution.

Characterization. The morphology of samples was observed under a Zeiss Ultra 55 field emission scanning electron microscope, with an accelerating voltage of 5 kV and InLens observation mode. The pore size data were evaluated from SEM micrographs by ImageJ (Fiji distribution).




b
5 µm
c
10 µm

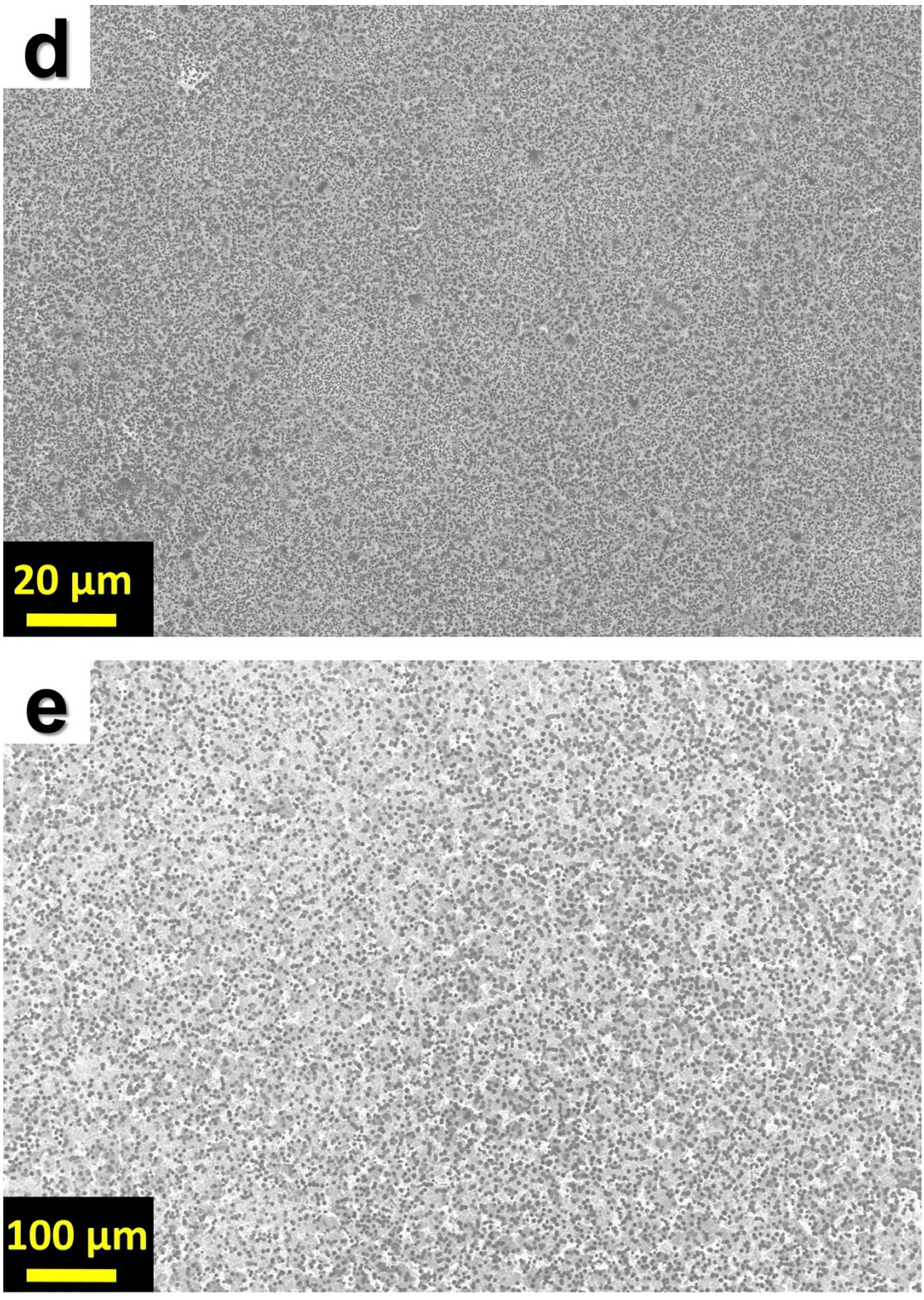


Fig. S1 Low magnification SEM images of MACE treated N-doped Si wafer etched in HF/HNO_3 aqueous solution for different time: (a) (b) 10 min, (c) 20 min, (d) 30 min, (e) 60 min.

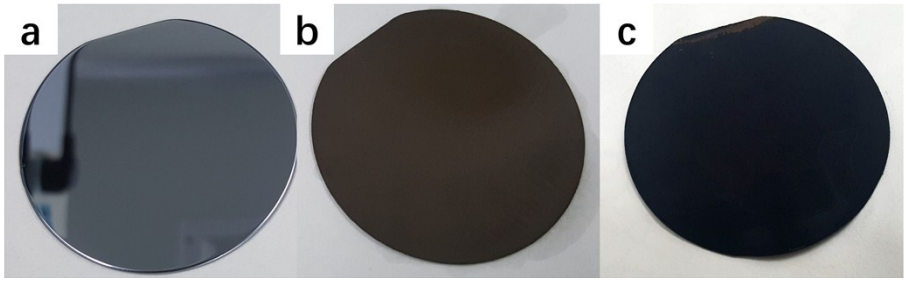


Fig. S2 Digital photos of (a) raw N-doped Si (100) wafer, (b) MACE treated wafer and (c) MACE plus 60 min HF/HNO_3 etched wafer.

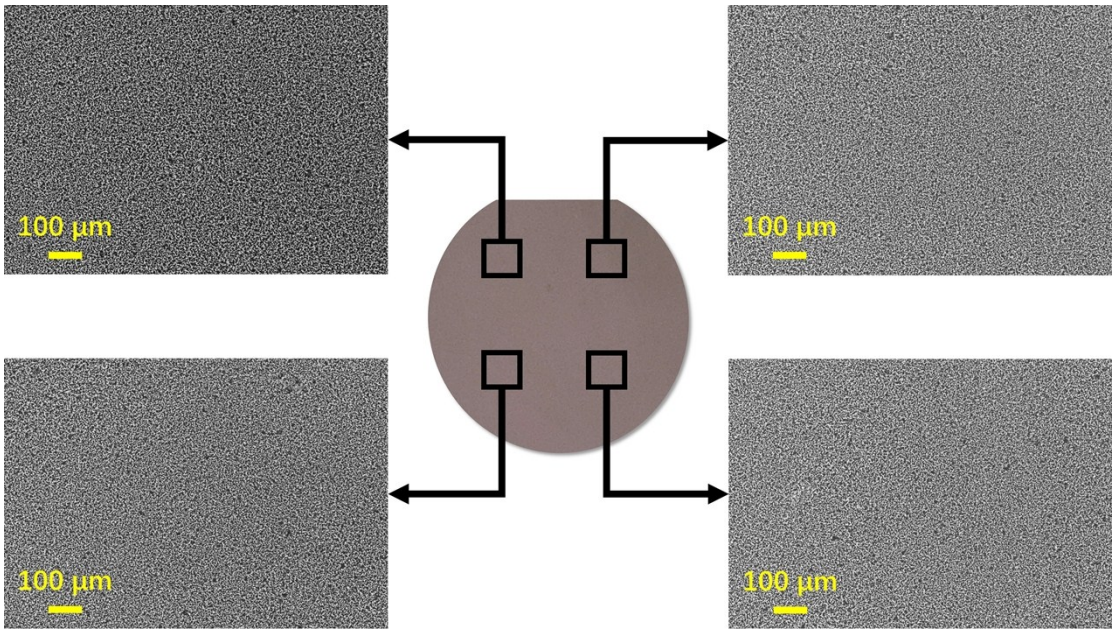


Fig. S3 SEM micrographs showing 4 different areas of a whole wafer treated by MACE. Each SEM image covers an area of about 2 mm^2.

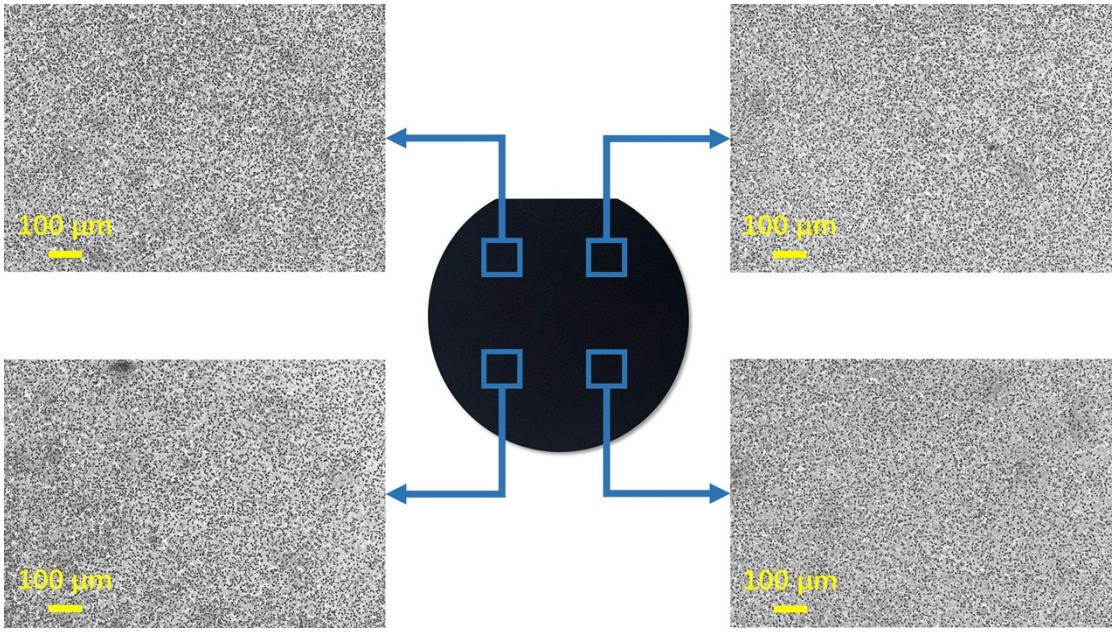
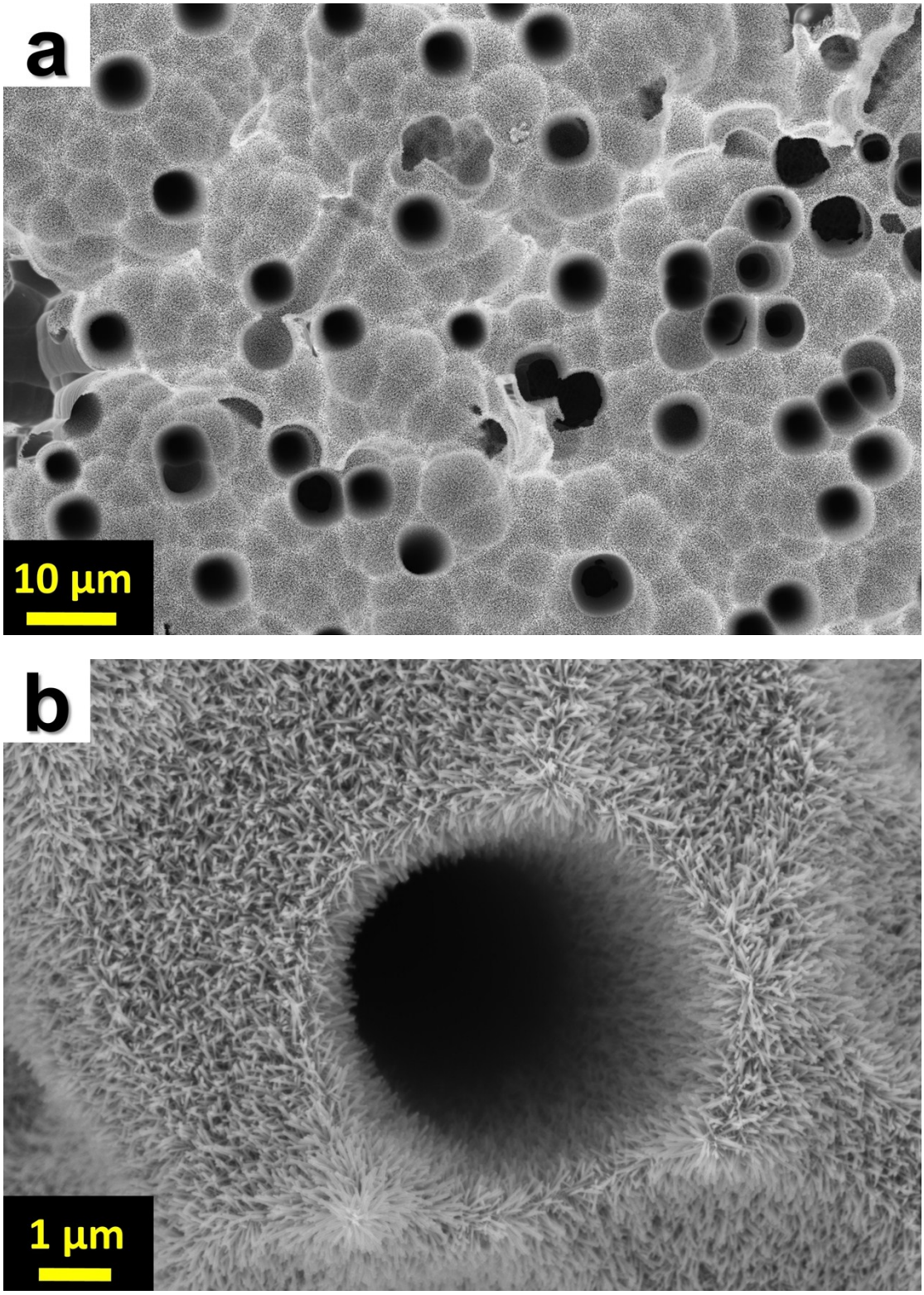


Fig. S4 SEM micrographs showing 4 different areas of a whole wafer treated by MACE plus 60 min HF/HNO_3 etching. Each SEM image covers an area of about 2 mm^2.


a
10 µm
b
1 µm

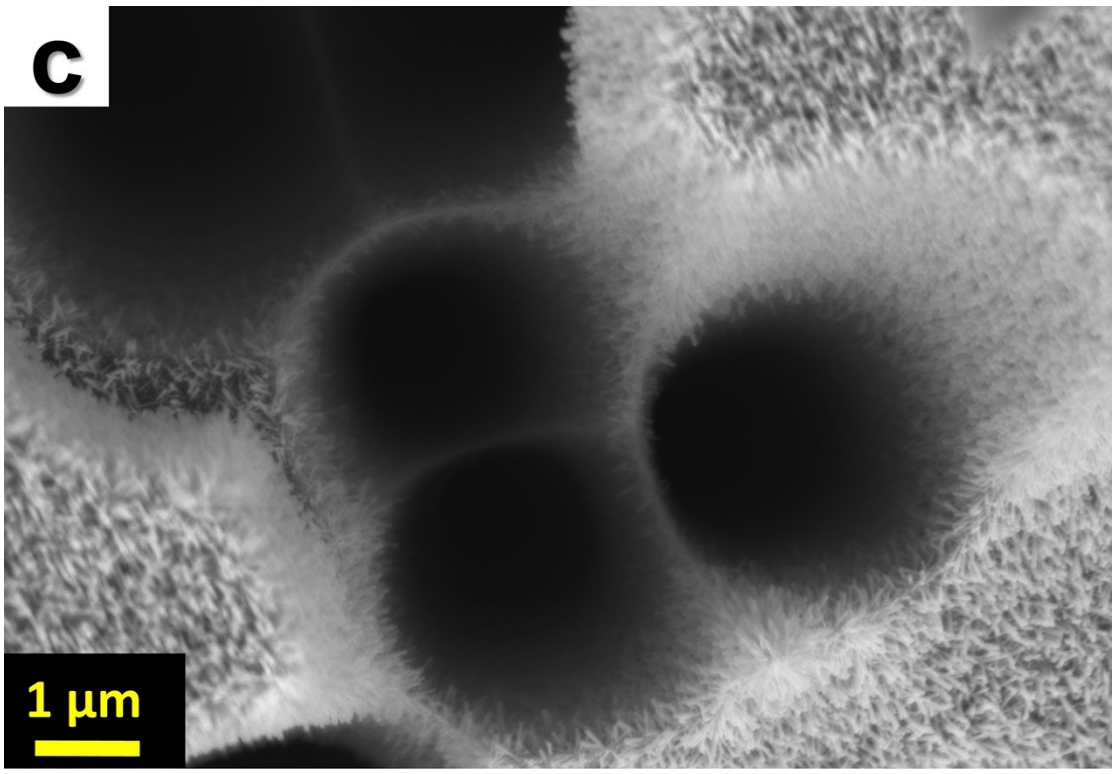


Fig. S5 Extra SEM data of 3D hierarchical porous structure of Si/ZnO: (a) 1000x magnifications showing the general morphology; (b)(c) 8000x magnifications showing nanowires grown inside the pores.

Fig. S6 Digital photos of HF/HNO_3 etching of control sample (left) and MACE treated wafer (right).

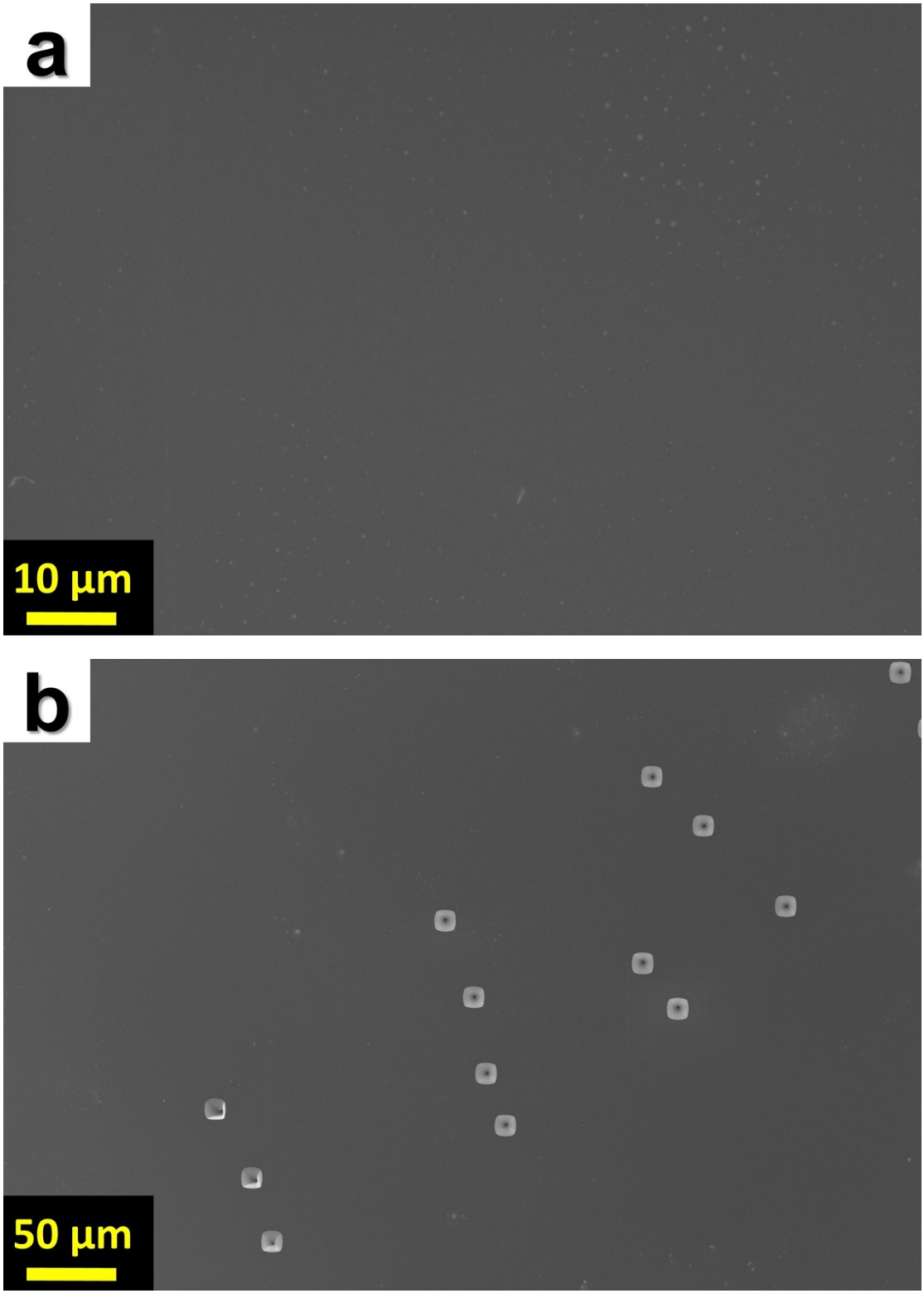


Fig. S7 (a) silicon wafer without MACE treatment after 60 min etching in HF/HNO_3, (b)isolated pores formed by etching initiated from the defects in intact silicon wafer surface

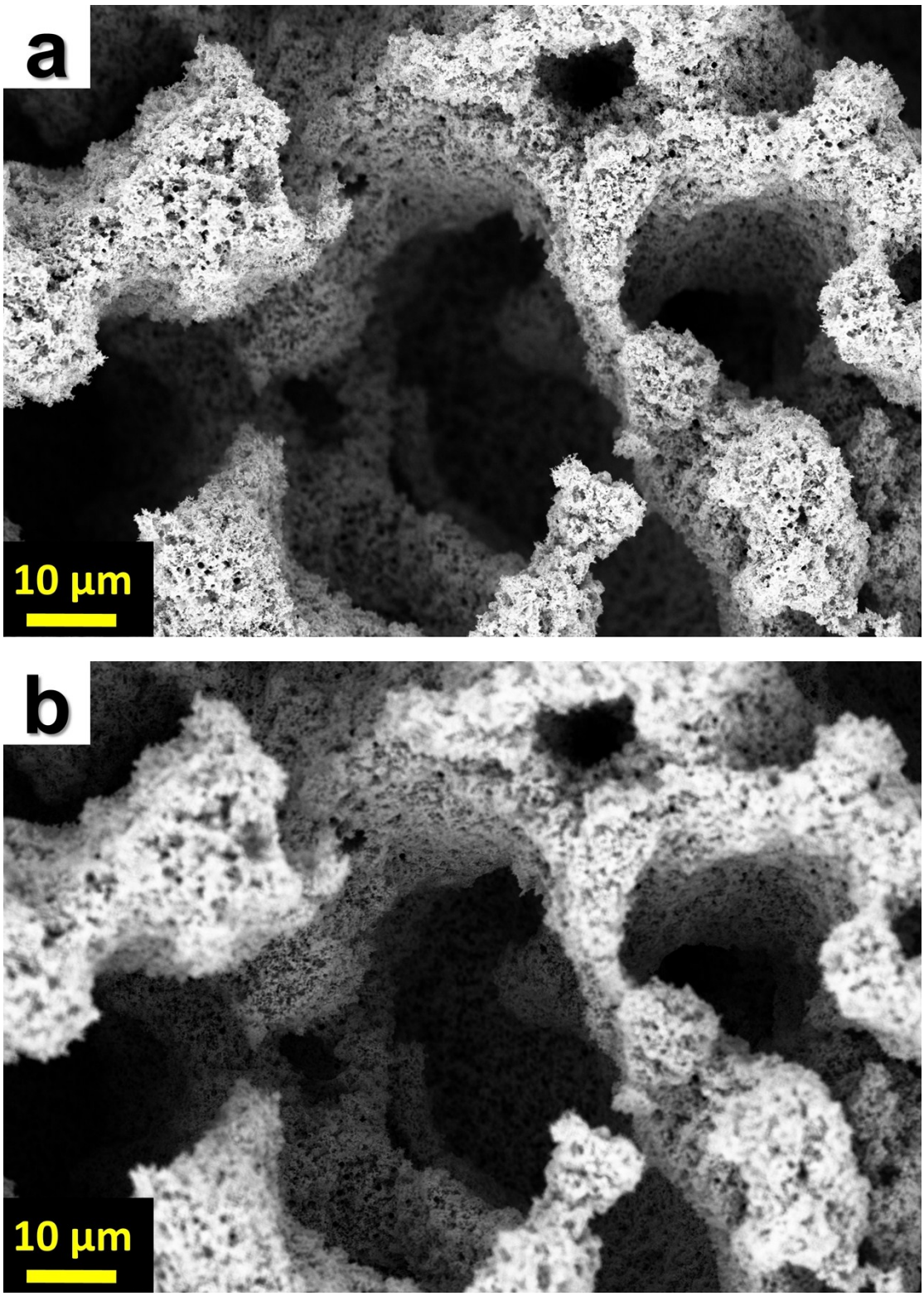


Fig. S8 SEM images of different focus in order to show (a) the exterior and (b) the interior porous structures formed by etching in HF/H_2O_2.

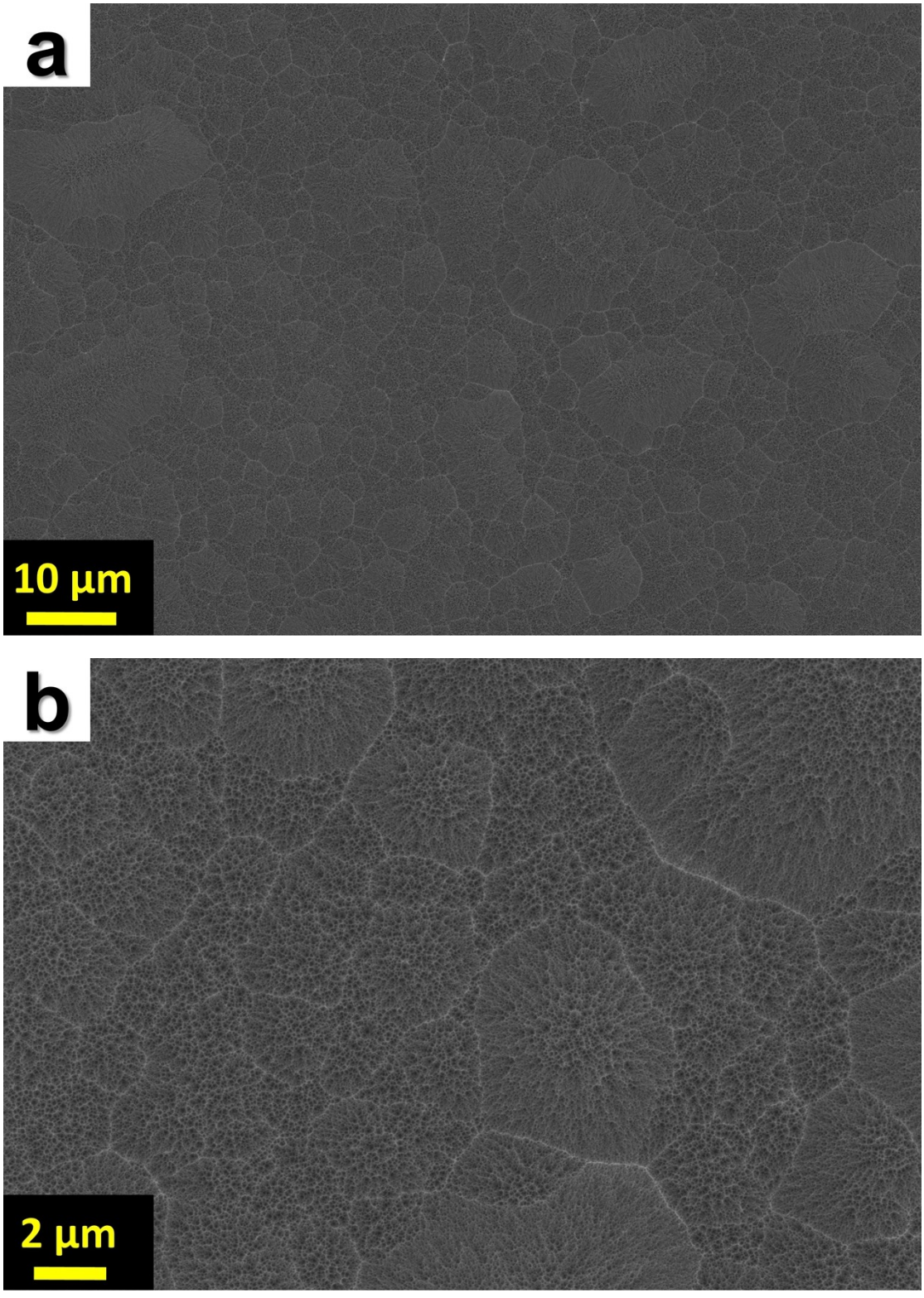


Fig. S9 Extra SEM data of densely packed pores fabricated from 30 min HF/HNO_3 etching of MACE treated P-doped Si wafer showing the general morphology: (a) 1000x magnification and (b) 4000x magnification.