Down to 7 nm pores in Si by photo-assisted electrochemical etching

Ferhat Aydinoglu and Bo Cui
Department of Electrical and Computer Engineering, University of Waterloo
200 University Ave. West, Waterloo, ON, N2L 3G1, Canada
faydinoglu@uwaterloo.ca

Deep silicon etching process has been well developed by using non-switching Bosch process or cryo-etching for fabricating high aspect ratio (protruded) pillar or line structures in nanoscale[1,2]. However, etching deep nanoscale recessed structures such as pores is more challenging because the etching gas/etching product would have difficulty to get into/out of the pores. Fabrication of high aspect ratio pores down to nanometer scale is possible using photo-assisted electrochemical etching that etches materials inside an electrolyte with applied electrical voltage. Here we show that, with optimized process, down to 7 nm diameter (200 nm depth) pores can be obtained using photo-assisted electrochemical etching[3].

In photo-assisted electrochemical etching, a silicon substrate is anodically biased and illuminated from backside of the n-type wafer to generate holes needed for silicon etching in a hydrofluoric acid (HF) based electrolyte (the etching setup is shown in Figure 1). The photo-generated electrons move towards the electrolyte through the external circuit, whereas the photo-generated holes move towards the silicon front side. A space charge region (SCR), which acts as a passivation layer with thickness dependent on the applied voltage and doping concentration, is formed at the Si/electrolyte interface. Generated holes diffuse towards the Si/HF interface and the cathode (platinum wire) supplies electrons to the electrolyte, leading to silicon dissolution at the interface. To form pores in Si substrate, the anodic current density J should be lower than the critical current density J_{PS}, which depends on the temperature and the electrolyte concentration. Current density below J_{PS} is called pore formation regime, and above J_{PS} is called electro-polishing regime. There is also a transition region observed between pore formation and electro-polishing regions[4-6]. By controlling the SCR width and the J_{PS} different pore and substrate morphologies can be obtained.

We studied systematically photo-assisted electrochemical etching of a bare silicon (0.9 Ωcm, (100), n-type) in hydrofluoric acid based electrolyte under different applied voltages and current densities at room temperature. The photo-current density was mainly controlled by adjusting the illumination intensity. We found out that when both applied voltage and current density are relatively high (about transition regime), a rough substrate with shallow pores was resulted (Figure 2a). Decreasing the current density to pore formation regime resulted in straight pores with better substrate morphology (Figure 2b). Here some of the pores are very shallow because hole carriers focus on sharper recessed pores on the substrate and competition among the pores leads to discontinued etching of some pores. When the voltage was decreased to 1.5 V while keeping the current density high, some random straight pores were formed (Figure 2c). When the voltage was kept the same yet the current density was greatly decreased, pores down to 7 nm diameter (~200 nm depth) were obtained (Figure 2d). Silicon with small (sub-10 nm diameter), deep or even through-thickness pores may find applications in nano-filtration[7] or as anode for lithium ion battery[8].

[1] H. Miao, A. A. Gomella, N. Chedid, L. Chen, and H. Wen. Nano Lett. 14, 6 (2014).
[2] C. Con, J. Zhang, and B. Cui. Nanotechnology 25, 17 (2014).
[3] V. Lehmann, H. Föll, J. Electrochem. Soc., 137(2), 653 (1990).
[4] R.L. Smith, S.D. Collins, J. Appl. Phys. 71, R1 (1992).
[5] X. G. Zhang, J. Electrochem. Soc. 136, 1561 (1989).
[6] B. Hamilton, Semicond. Sci. Technol. 10, 1187 (1995).
[7] M. Ulbricht. Polymer 47, 7 (2006).
[8] J. H. Cho, and S. T. Picraux. Nano Lett. 13, 11 (2013).

Down to 7 nm pores in Si by photo-assisted electrochemical etching

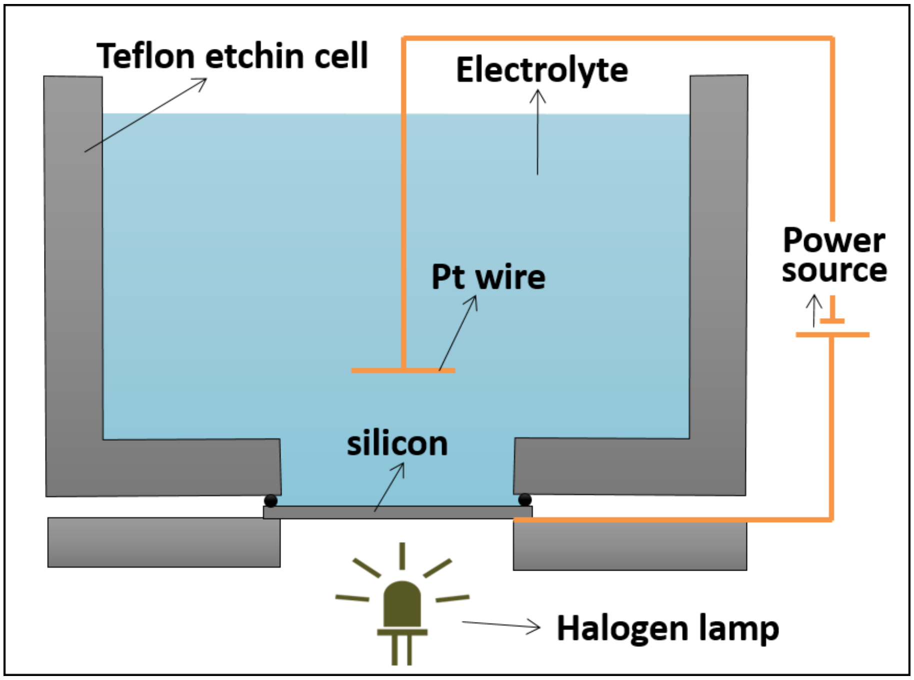

Figure 1. Setup for the photo-assisted electrochemical etching of silicon.

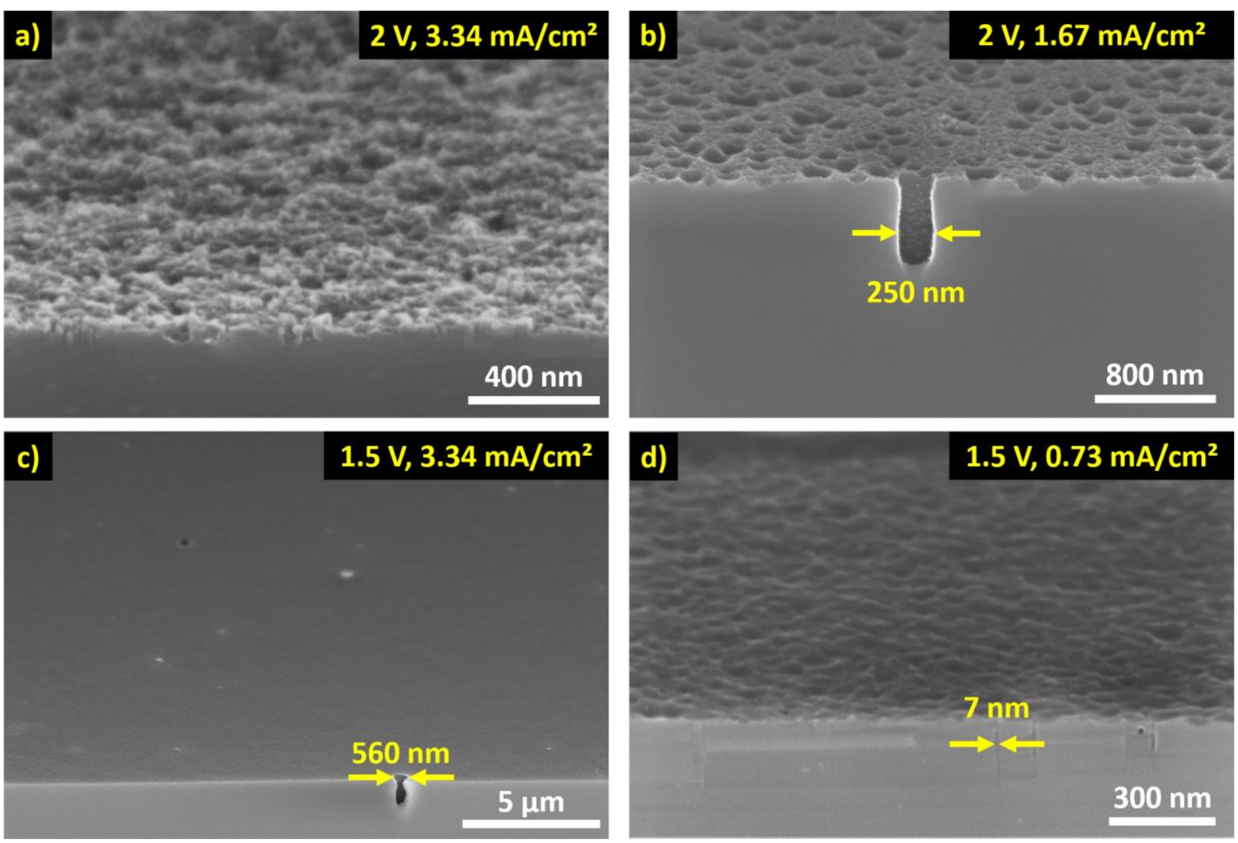

Figure 2. SEM images of porous silicon etched under different applied voltages and current densities as indicated in the images.