Supporting Information

A Tunable Sub-100 nm Silicon Nanopore Array with an AAO Membrane Mask: Reducing Unwanted Surface Etching by Introducing a PMMA Interlayer

Namsoo Lim,^a Yusin Pak,^b Jin Tae Kim,^c Youngkyu Hwang,^b Ryeri Lee,^b Yogeenth Kumaresan,^b NoSoung Myoung,^d Heung Cho Ko,^b and Gun Young Jung^{*a,b}

^aDepartment of Nanobio Materials and Electronics, ^bSchool of Materials Science and Engineering, and ^dAdvanced Photonics Research Institute, Gwangju Institute of Science and Technology (GIST), 123, Cheomdan-gwagiro, Buk-gu, Gwangju, 500-712, South Korea

^cCreative Future Research Laboratory, Electronics and Telecommunications Research Institute, 218, Gajeong-ro, Yuseong, Daejeon 305-700, South Korea

Corresponding e-mail address: gyjung@gist.ac.kr



Fig. S1. (a) The thickness of the AAO NP membrane measured by a cross-sectional SEM image and alpha-step; second anodizing time was 300 s. After peeling the AAO membrane off the un-reacted aluminum, it was placed on a silicon substrate to measure the thickness. Both results show almost the same value of 300 nm. **(b)** AAO NP size variation with the pore-widening (PW) time in H_3PO_4 aqueous solution; PW was performed for different times of 22 min, 23 min, 25 min, 26 min, 27 min, 30 min, 32 min, and 35 min. **(c - j)** After the PW process, the bottom side of each AAO membrane was checked by the SEM. In each image, 20 NPs were selected randomly, and their diameters were measured. When the PW time was less than 22 min, the barrier layer could not be completely eliminated. The average NP size increased with the pore-widening time. After 30 min, the neighboring NPs began to touch.



Fig. S2. I. Homemade contact printing system utilized in this paper; (a) Sample stage with a PDMS (polydimethylsiloxane) sample holder that could apply a hydraulic pressure to the sample. (b) Hotplate was placed on top of the sample sealed by vacuum along the groove on the sample stage. (c) Temperature controller. (d) Pressure gauge. (b) System controller. II. After the sample loading, the upper chamber was slid down and tightly chucked prior to applying highly compressed nitrogen gas.



Fig. S3. Optical images of the transferred AAO NP membranes onto the PMMA-coated silicon wafer; (a) 0.5 cm \times 0.5 cm-sized AAO membrane was well transferred. (b) A relatively large-sized AAO membrane (1 cm \times 1 cm) was transferred with unwanted (c) air-traps and (d) wrinkles. The images of (c) an air trap and (d) wrinkles were taken by an optical microscope and a scanning electron microscope (SEM), respectively.



Fig. S4. (a) Thickness of the spin-coated PMMA layer measured by alpha-step. The value was approximately 20 nm. **(b)** Cross-sectional SEM image of the AAO NP membrane/PMMA/Si structure after the contact printing (CP) process. **(c)** Top view of the PMMA layer after the CP process; The AAO NP membrane was selectively eliminated by wet-etching in a 5 wt% H_3PO_4 aqueous solution. Due to the high pressure introduced during the contact printing, a nano-embossing pattern was generated on the PMMA layer. **(d)** The transferred PMMA nano-mesh pattern generated at the step of O_2 plasma etching, showing a smooth PMMA surface. **(e)** The PMMA layer after subsequent silicon etching with CF₄ plasma, showing pin-holes that were attacked by reactive neutral species and ions. **(d)** and **(e)** were performed using the AAO NP membrane as a mask. These pictures were taken after removing the AAO NP membrane mask. **(f)** Silicon nanopore (SiNP) array after eliminating the sacrificial PMMA layer, showing a smooth silicon surface that was protected by the PMMA interlayer during the plasma etching and **(g)** its cross-sectional view with a height of 22 nm.



Fig. S5. Silicon nanopore (SiNP) arrays with different pore diameters of sub-100 nm. To demonstrate the apparent pore size-control of the SiNPs, three different pore-sized AAO membranes were used as etching masks. The pore-widening times were 23 m, 26 m, and 30 m, respectively. 7 NPs were selected in each SEM image, and the pore-diameters were measured to give an average diameter of (a) 59.5 nm, (b) 75 nm and (c) 85.9 nm, respectively. The average diameter of the SiNPs increased with the pore widening time of the AAO NP membrane.