Electronic Supplementary Information for

Three-dimensionally designed Anti-reflective Silicon Surfaces for Perfect Absorption of Light

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1. Experimental Methods

1.1 Fabrication of 3D Hierarchical Silicon Surfaces

The 3D reflective silicon (Si) surfaces were produced by a hybrid fabrication process involving a maskless silicon etching process, a pillar self-assembly process, and nanostructure synthesis. Figure 1 schematically illustrates the fabrication method and shows scanning electron microscopy (SEM) images of each step.

Fabrication of the Si micropillars used a deep reactive-ion etching (DRIE) process based on the "black silicon" method.[1–4] The procedure is described as follows. First, cleaned and polished 4-inch silicon wafers were prepared (P-type <100>). No pre-processing, such as lithography, was used. The wafers were subjected to a pulsed etching process that used alternate cycles of etching and passivation using an inductively coupled plasma multiplex system (Surface Technology Systems Ltd., UK). In the etching cycle, sulphur hexafluoride (SF_6) and oxygen (O_2) gases flowed at 130 sccm and 13 sccm, respectively. In the passivation cycle, the octafluorocyclobutane (C_4F_8) gas flow rate was 85 sccm. Coil power and platen power were 600 and 30 W, respectively. Switching times for the etching and passivation cycles were 6 and 4 s, respectively. Bias voltage was 120 and 0 V for etching and passivation, respectively. The total process time was 3000 s. Under these conditions, Si micropillars with high aspect ratios (width: 100 nm (apex), 1 μm (base); length: 20 μm) formed sparsely as shown in Figures 1(d) and 2(a).

Dilute chemical polymerisation was used to coat the Si micropillars with a PANI nanostructure.[5–7] The micro-structured silicon chip was immersed in an aqueous solution containing 1 M $HClO_4$ (Samchun Pure Chemical Co., Korea), 6.7 mM ammonium persulfate (APS, Sigma Aldrich Co., USA) and 10 mM aniline monomer (Sigma Aldrich Co., USA). The aniline monomer was polymerised at 0–4°C while shaking for 12 h. The Si substrates were then rinsed in a deionised (DI) water flow to remove the remaining PANI residue. The membranes were then dried in a flow of N_2 gas and placed in a desiccator for 1 day. As the aqueous solution evaporated, capillary forces between the free ends of the micropillars caused them to deform and adhere to each other. The morphology of the self-assembled structure can be modified by controlling the design parameters such as surface tension and stiffness.[8] The final self-assembled nanostructure-coated micropillar structures are shown in Figures 1(e) and 2(b–d).

1.2 Evaluation of Optical Properties

SEM measurements were carried out using a field-emission SEM instrument (SU-6600, Hitachi, Japan). Optical reflectance measurements of the micro-/nano-structured surface were conducted using a UV–visible–NIR spectrophotometer (Cary 5000, Varian, USA) equipped with absolute specular and hemispherical reflectance accessories (SRA and DRA, respectively). To measure the total reflectance using the hemispherical reflectance accessory, the incident angle was changed from 90° (normal) to 93° 20'. Reflectance was measured from the UV range (300 nm) to the NIR range (2000 nm) to examine the effect of the silicon nanostructures on broadband reflectance.[9,10]

1.3 Evaluation of Wetting Properties

Characterisation measurements: Contact angle (CA) and sliding angle (SA) were measured according to the trajectory of 4-μL DI water droplets with respect to the nanostructured surface, using a droplet-shape analysis system (Smart Drop, Korea) and the sessile droplet method.

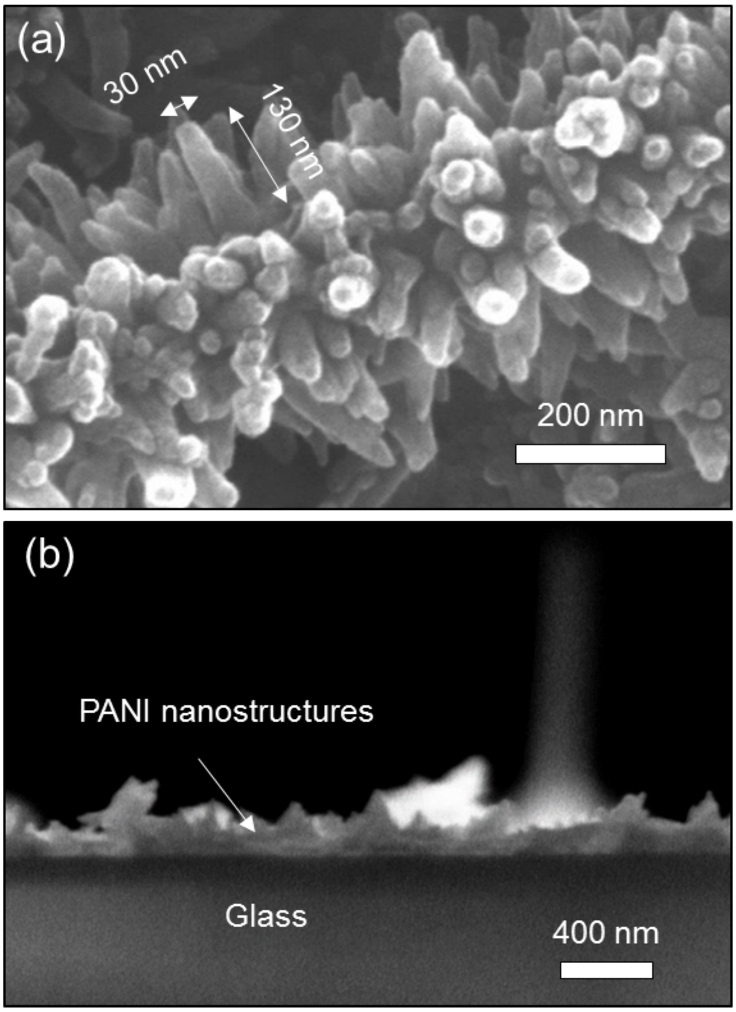

Fig. S1 Magnified SEM images of the PANI nanostructure. (a) The PANI nanostructure had a sub-wavelength architecture with diameters of 20–40 nm and a length of ca. 100 nm. (b) Cross-sectional view of the PANI nanostructured layer on a glass substrate.

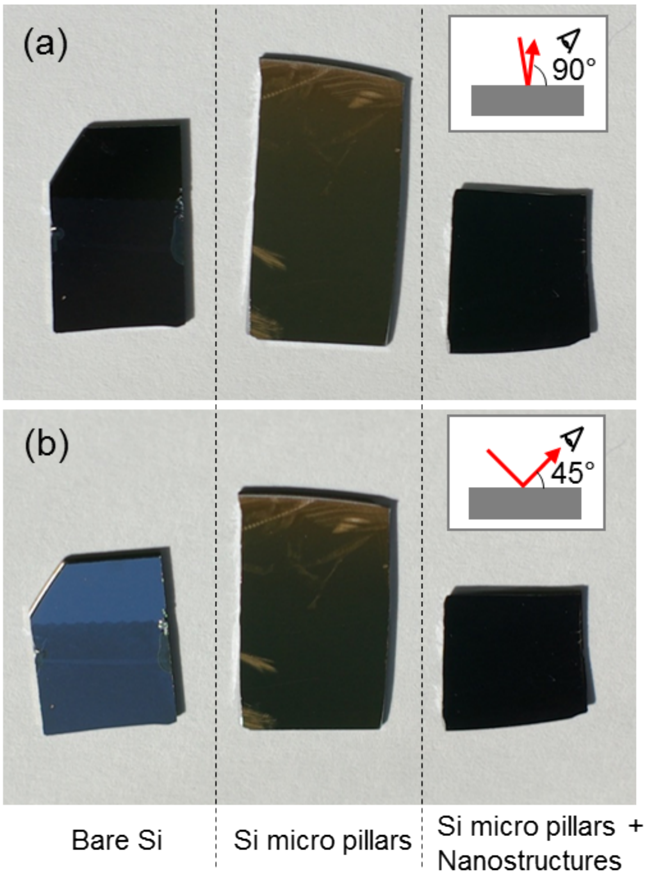

Fig. S2 Optical images of polished, 1D micropillar, and 3D hierarchical surfaces at incident angles of (a) 90°, and (b) 45°.

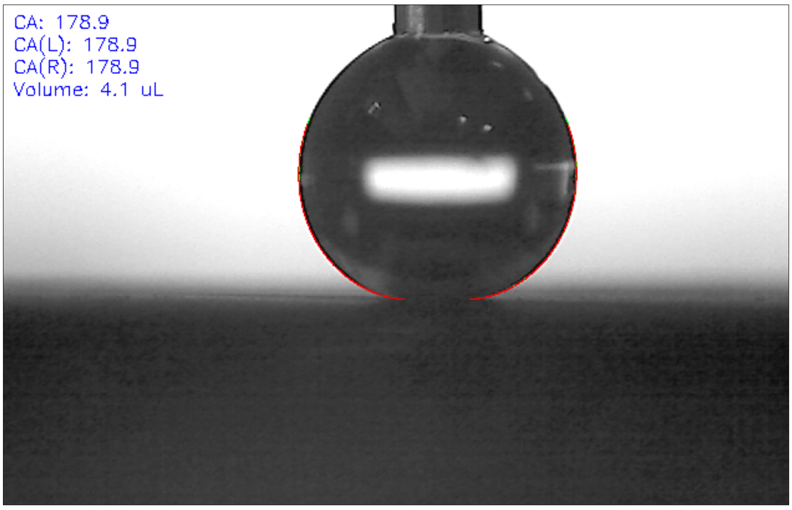

Fig. S3 Anti-wettability test of the 3D hierarchical surfaces with a 4-μL sessile water drop (static water contact angle = 179º and sliding angle < 1º).

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