Supporting Information for

Superhydrophobic Nanostructured Silicon Surfaces with Controllable Broadband Reflectance

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Experimental details

Fabrication: Silicon nanostructures, referred to as nanograss, were fabricated using a deep reactive-ion etching (DRIE) process based on the "black silicon" method.^{1–3} First, cleaned and polished 4-inch silicon wafers were prepared (P-type <100>, $0.01-0.02 \Omega$). No preprocessing, 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, sulfur hexafluoride (SF₆) and oxygen (O₂) gases flowed at 130 sccm and 13 sccm, respectively. In the passivation cycle, the octafluorocyclobutane (C₄F₈) gas flow rate was 85 sccm. Coil power and platen power were 600 W and 30 W, respectively. Switching times for the etching and passivation cycles were 6 s and 4 s, respectively. Bias voltage was 120 V and 0 V for etching and passivation, respectively. Under these conditions, nanograss with high aspect ratios (width: 50–3000 nm, length: $0.1-50 \mu$ m) formed sparsely. The morphology was controlled by varying the total process time from 100 s to 5000 s. After etching, the surface was passivated with a fluoropolymer layer, which had low surface energy, for 10 s by plasma polymerized fluorocarbon coating (PPFC) using the same system as DRIE. Finally, the nanostructures possessed superhydrophobicity (CA: >160°) because of their tip-shaped nanostructured topography and chemically modified surfaces.

Characterization: Scanning electron microscopy (SEM) measurements were carried out on a field-emission (FE)-SEM instrument (SU-6600, Hitachi, Japan). SEM images of nanograss were acquired by tilting the sample 0°, 30°, and 90° to confirm the width, length, and morphology. Contact angles (CAs) were measured between 3-µL deionized water droplets and the nanostructured surface using a drop-shape analysis system (DSA 100, Kruss, Germany) in the sessile drop method. Optical reflectance measurements on the nanostructured surface were conducted using an ultraviolet–visible–infrared (UV– Vis–IR) spectrophotometer (Cary 5000, Varian, USA) with an absolute specular reflectance accessory. Reflectance was measured from the UV range (wavelength: 200 nm) to the IR range (3000 nm) to examine the effect of silicon nanostructures on broadband reflectance.



Fig. S1 SEM images of nanostructured surfaces on 3D silicon surfaces. The DRIE process is an integrated circuit (IC)-compatible processes for solar cell and microelectromechanical systems (MEMS) devices.



Fig. S2 Various morphologies of nanograss as a function of process time. (A, B) 0° and 90° tilted SEM images of nanograss at process times of 1000 s, respectively. (C, D) Process time of 2000 s. (E, F) Process time of 3000 s. (G) Density and length dependence on process time. Nanograss began to form at ~600 s. Length increased with increasing process time, but the density became saturated at 900 s.

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