

Supplementary Information

Hydroxyl functionalization improves the surface passivation of nanostructured silicon solar cells degraded by epitaxial regrowth

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Methods

(1) Fabrication of nanostructured (NS) Si solar cells

Czochralski-grown (CZ) Si (100) wafers (p-type, $\rho = 1\text{-}5 \text{ }\Omega\cdot\text{cm}$) were etched using potassium hydroxide solution (46 %) at 80 °C for 70, 80 and 90 min, producing 200, 100 and 50 μm -thick substrates, respectively. Thin c-Si substrates were prepared after standard RCA (Radio Corporation of America) cleaning following piranha ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) and HF (HF:H₂O) solutions. In order to form nanostructured (NS) Si arrays, silver nanoparticles (NPs) were precipitated uniformly for 15 s using galvanic displacement reaction employing an aqueous solution of HF (4.8 M) and AgNO₃ (0.005 M). The NS Si was allowed to form at room temperature using a mixed solution of HF (4.8 M) and H₂O₂ (0.44 M). The diameter of the NS Si was between 40 and 60 nm and the lengths of nanostructures were adjusted by varying the etching time. Residual Ag NPs were then removed using concentrated nitric acid (30 wt%) for 30 min, and the NS Si arrays were finally rinsed with de-ionized water. To fabricate NS

Si solar cells, the emitter layer was formed by phosphorus diffusion via a spin-on-dopant (SOD) method. The SOD doping was performed after nanostructuring. Phosphorous silicate precursors (P509, Filmtronics) were spun onto wafers, and n⁺-emitter formed using the mixture of N₂ and O₂ via thermal diffusion of gaseous phosphorous at 830°C for 26 min. The phosphorus glass that remained after SOD diffusion was removed using a diluted HF solution. The front contact (Ti/Ag) on n⁺-emitter layer and back contact (Al) electrodes were formed by electron-beam evaporation. An oxygen plasma process was fulfilled in 50 W (the minimum power to generate plasma) due to avoiding plasma-induced surface damages. The gas flow, pressure and process temperature were 200 sccm, 100 mTorr and 30 °C, respectively. A ~15 nm-thin Al₂O₃ film produced via atomic layer deposition (ALD) process using Al(CH₃)₃ as a metal precursor and H₂O as an oxidant. Post-annealing was performed at 425 °C for 30 min in the ambient of forming gas (a mixture of 90% N₂ + 10% H₂).

(2) Measurement and characterization

The interface structure of Al₂O₃/nanostructured Si was characterized using field-emission transmission electron microscope (FE-TEM, JEOL JEM-2100F) equipped with a field-emission gun. The electron energy-loss spectroscopy (EELS) in a high-resolution TEM was utilized with a high-energy resolution of 0.5 eV. The backgrounds in each EEL spectrum are subtracted using a power-law model.¹ The passivation ability of Al₂O₃ is evaluated by looking at variations of the effective carrier lifetime (τ_{eff}) measured by quasi-steady-state photoconductance (QSSPC, WCT-120). Using an IR-pass filter (RG 850, passing wavelengths longer than 850 nm), a light source induces photogenerated carriers in the Si substrates. Then, τ_{eff} at a minority carrier density (MCD) of $1 \times 10^{15} \text{ cm}^{-3}$, which corresponds to a typical carrier concentration for solar cells at an illumination of 1 sun, can be used to calculate surface recombination velocity (SRV, cm/s) and carrier diffusion length (L),

respectively. Micro-Raman spectra were recorded using a LabRAM HR 800 spectrometer that was equipped with a confocal microscope in the backscattering configuration. An excitation source (i.e., an Ar-laser operating at 514 nm with a power of $0.05 \text{ mW}/\mu\text{m}^2$ and a spot diameter of $\sim 25 \mu\text{m}$) was utilized to prevent local heating.² The laser beam was focused by the Olympus objective indicating 0.5 of numerical aperture. Optical reflection measurements were performed between the wavelengths of 400 and 1000 nm using a UV-Vis/NIR spectrophotometer (Lambda 750, Perkin Elmer) equipped with a 60 mm integrating sphere (Labsphere) to account for total light (diffuse and specular) reflected from the samples

S1. High resolution TEM images of nanostructured (NS) Si arrays with Al_2O_3 films

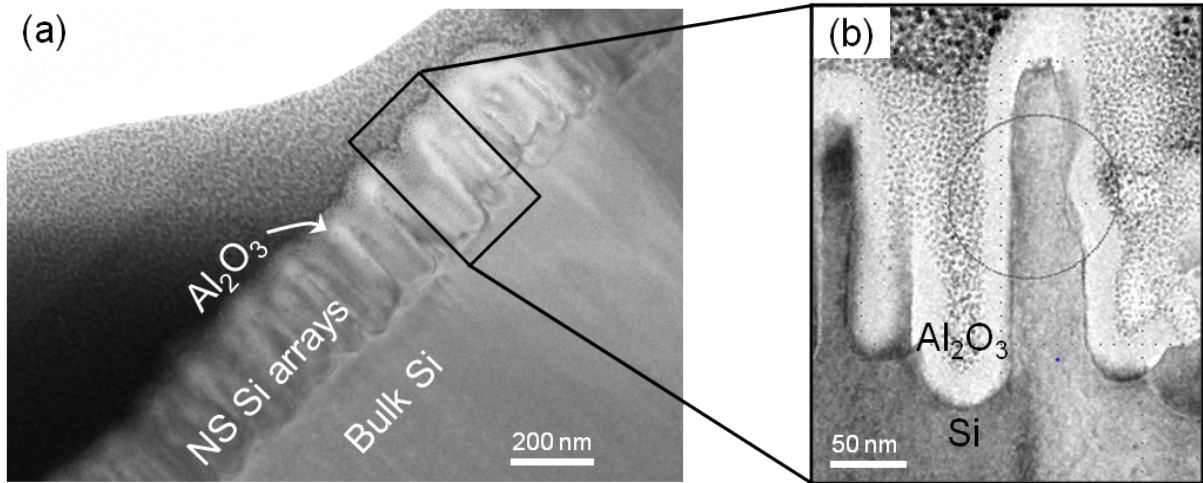
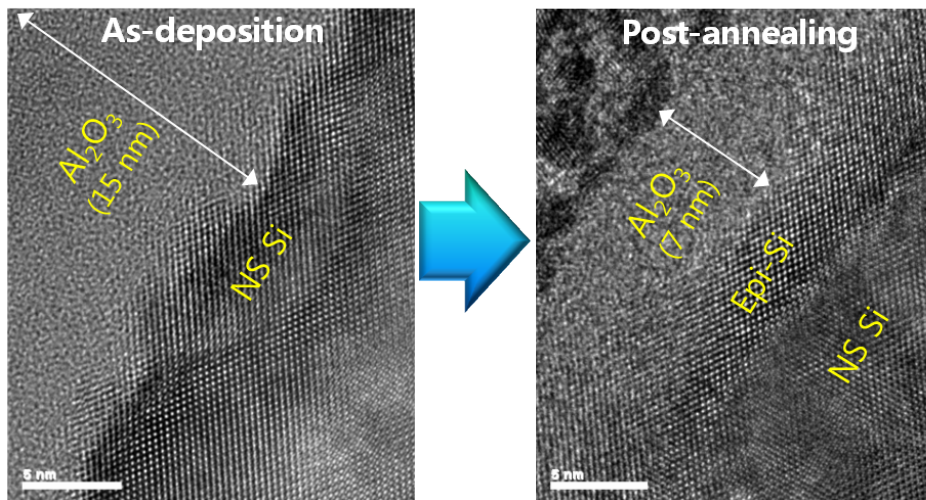


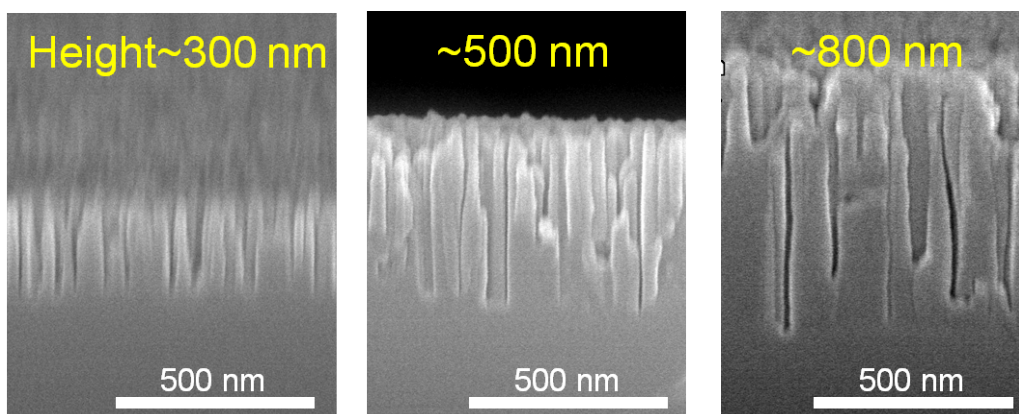
Figure S1. (a) Cross-sectional TEM image (low-magnified) showing the NS Si arrays coated by Al_2O_3 films. (b) A magnified view of a rectangle shown in panel a. Panel b is the identical image displayed in Figure 1b of the manuscript text.

S2. High resolution TEM images of the Al₂O₃/NS Si interface upon post-annealing



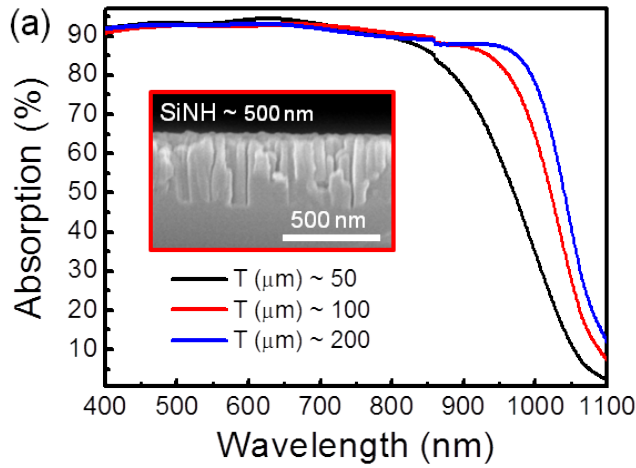
Figures above compares the morphological change upon post-annealing, in which the thickness of Al₂O₃ decreases from ~15 (as-dep) to ~7 nm (annealed) owing to the epitaxial regrowth of Si into the Al₂O₃.

S3. Cross-sectional FESEM images with the varied heights of NS Si



NC Si arrays were formed using metal-assisted chemical etching (MaCE). Heights of NC Si has been controlled from 300~800 nm as the etching time was adjusted from 20~70 s.

S4. Light absorption of NS Si arrays (height=500 nm) as a function of wafer thicknesses (50, 100, and 200 μm)



(b)

Wafer thickness (nm)	Ave. absorption from 400 to 1100 nm (%)
50	75
100	81
200	84

When the wafer thickness decreases from 200 to 50 μm , light absorption normally decreases (as expected), as shown in Figure S3a. This is especially true at longer wavelengths between 800 and 1100 nm. Figure S3b lists the average light absorption (%) measured between 400 and 1100 nm.

References

1. R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, Plenum Press, New York, USA, 1996.
2. R. Gupta, Q. Xiong, C. K. Adu, U. J. Kim, P. C. Eklund, *Nano Lett.*, 2003, **3**, 627-631