Supporting Information

Long-term durable silicon photocathode protected by a thin Al₂O₃/SiOₓ layer for photoelectrochemical hydrogen evolution

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Experimental Details

Materials: Boron-doped (p-type) single crystal Si wafers (4-inch-diameter, 525±15 μm thickness, normal doped with 1.0–10.0 ohm·cm resistivity, (100) oriented) were purchased from Silicon Technology Corporation. AgNO₃ (99.8%) was obtained from Dae Jung Chemical, and HF (48–51 wt%) was obtained from J.T. Baker. Concentrated nitric acid solution (64–66 wt%) was obtained from Duksan Pure Chemicals.

Fabrication of Nanoporous Si Photocathode: The Si wafers were cut into four pieces, and the back
side of each piece was covered with a HF-proof masking layer (Microstop, Pyramid Plastics, INC) to prevent etching on both sides of the Si wafers by HF. In order to remove a native oxide formed on the Si surface, the Si substrates were first dipped into an aqueous HF solution for 2 min. Nanoporous silicon (Np-Si) electrodes were fabricated by a modified metal-catalyzed electroless etching (MCEE) method. The Si substrates were plated with silver nanoparticles (Ag NPs) by a galvanic displacement reaction in a mixed solution of AgNO₃ (0.005 M) and HF (4.8 M) for 1 sec. After the Ag NP seeds were formed, MCEE was carried out with a mixed solution containing HF (4.8 M) and H₂O₂ (0.6 M) in deionized water for 30 sec at room temperature. The resulting nanoporous Si electrode was then thoroughly washed with deionized water. Excess Ag residues were completely removed by dipping the electrode in concentrated nitric acid solution for 20 min.

**Deposition of the Al₂O₃ passivation layer and Pt:** In order to deposit the Al₂O₃ passivation layer onto the bare and nanoporous Si electrodes, the electrodes were first cleaned by dipping in an aqueous HF solution to remove the native oxide that had formed on its surface. A thin Al₂O₃ layer was deposited in a layer-by-layer fashion onto the Si electrode by atomic layer deposition (ALD, LUCIDA D100). The deposition was performed using successive pulses of trimethylaluminum (TMA) and deionized water under a nitrogen carrier gas in a vacuum chamber heated at 230 °C. The thickness was measured using spectroscopic ellipsometry (Sopra GES 5E, fitted to a Tauc-Lorentz function) and transmission electron microscopy (TEM). The Pt catalyst was deposited by sputtering (Q150R S Sputter Coater, Quorum) at a current of 20 µA for 5 s.

**Characterization:** Scanning electron microscopy (SEM) was carried out using a field-emission scanning electron microscope (Hitachi S-4800 FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector. TEM was carried out using a JEOL 2010F at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI Versa Probe system with a 100 W Al K Alpha X-ray source with a spot size of 400 µm at a 45° incident angle. The reflection spectra of the Si specimens were measured using a Perkin Elmer Lambda 750 UV/VIS/NIR spectrophotometer with an integrating sphere (Labsphere) in a wavelength range of 300–
1200 nm, which corresponds to the major spectral irradiance of sunlight. The minority carrier lifetimes were measured using a silicon wafer lifetime tester (WCT-120, Sinton Instruments).

**Photoelectrochemical measurement:** Photocurrent-photovoltage ($J-V$) responses were recorded using a potentiostat (Iviumstat) at a scan rate of 50 mV/s in a three-electrode configuration using Pt gauze as a counter electrode and an Ag/AgCl reference electrode. An aqueous H$_2$SO$_4$ solution (0.5 M) was employed as an electrolyte. Prior to the photocurrent measurement, the electrolyte was thoroughly purged with N$_2$ gas for 10 min to expel O$_2$ dissolved in the H$_2$SO$_4$ solution and kept purged during the measurement to ensure O$_2$-free electrolyte. In order to form an ohmic contact between a copper plate and the fabricated Si photocathode, gallium-indium eutectic (Sigma-Aldrich) was spread onto the back side of the photoelectrode. The area of the Si electrode exposed to the electrolyte was 0.38 cm$^2$. Photoelectrochemical performance of the Si electrodes was investigated under the illumination of AM 1.5G (100 mW/cm$^2$) using a solar simulator (Peccel PEC-L11). The potentials were rescaled to the potentials versus the reversible hydrogen electrode (RHE) according to the following equation: $E$ (RHE) = $E$ (Ag/AgCl) + 0.197 V at pH 0.
**Fig. S1** XPS survey spectrum of Al₂O₃/bare Si photoelectrode.

**Fig. S2** Atomic percentages of Si 2p (black), O 1s (red) and Al 2p (blue) as a function of electron take-off angle determined by the XPS analysis of an Al₂O₃/bare Si photoelectrode.
**Fig. S3** XPS spectra of Si 2p from Si photocathode before the ALD of a thin Al₂O₃ layer.

**Fig. S4** Schematic illustration of electrode structure of Al₂O₃/bare Si photoelectrode.
Fig. S5 J-V curves of the Al₂O₃/bare Si photoelectrodes as a function of Al₂O₃ thickness (different samples). Note that J-V curves of Si photoelectrodes slightly vary from sample to sample, but the same overall trend in overpotential change as a function of Al₂O₃ thickness was observed for multiple samples.

Fig. S6 Long-term stability test of (a) bare Si and (b) Al₂O₃(2.3 nm)/bare Si photoelectrodes at -0.9 V vs. RHE under AM 1.5G (100 mW/cm²) illumination (different samples).
Fig. S7 TEM images of Al₂O₃/bare Si photoelectrode after 12 h long-term test.
Fig. S8 (a) TEM images of Al₂O₃/bare Si photoelectrode (a different sample was used to affirm the Pt deposition) after 12 h long-term test and (b) EDS point analysis.
Fig. S9 XPS spectrum of Al 2s from Al₂O₃/bare Si photoelectrode after 12 h long-term test. Note that Al 2s spectrum was collected instead of Al 2p spectrum because of the peak overlap of Al 2p and Pt 4f.

Fig. S10 SEM and TEM images of nanoporous Si photoelectrode.
**Fig. S11** Reflectance spectra of bare Si (black), Np-Si (green), Al₂O₃/Np-Si (blue) and Pt/Al₂O₃/Np-Si (red).

**Fig. S12** $J$-$V$ curves of the bare Si, Al₂O₃/bare Si, Np-Si, and Al₂O₃/Np-Si photoelectrodes (different samples). Note that $J$-$V$ curves of Si photoelectrodes slightly vary from sample to sample, but the same overall trend in overpotential change was observed for multiple samples.
**Fig. S13** Chopped photocurrent measurement of Np-Si (Black) and Al$_2$O$_3$/Np-Si (Red). The bias potential of 0.3 V with respect to RHE was applied for 8 s (4 s with light ON and 4 s with light OFF).
Fig. S14 Long-term stability test of (a) Np-Si and (b) Al$_2$O$_3$/Np-Si photoelectrodes at -0.9 V vs. RHE under AM 1.5G (100 mW/cm$^2$) illumination (different samples). Note that the performance of Si photoelectrodes slightly vary from sample to sample, but the same trend in long-term stability was observed for multiple samples.
Fig. S15 TEM images of Pt nanoparticles deposited on Np-Si photoelectrode.

Fig. S16 $J$-$V$ curves of the Np-Si, Al$_2$O$_3$/Np-Si, Pt/Np-Si, and Pt/Al$_2$O$_3$/Np-Si photoelectrodes (different samples). Note that $J$-$V$ curves of Si photoelectrodes slightly vary from sample to sample, but the same overall trend in overpotential change was observed for multiple samples.