11.5% efficiency of TiO_2 protected and and Pt catalyzed n^+np^+-Si photocathodes for photoelectrochemical water splitting: manipulating the Pt distribution and Pt/Si contact

Zhihao Yin, Ronglei Fan, Guanping Huang and Mingrong Shen*

College of Physics, Optoelectronics and Energy, Jiangsu Key Laboratory of Thin Films, and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, 1 Shizi street, Suzhou 215006, China

Supporting Information

Experimental details:

Fabrication of n^+np^+-Si:

Single-crystalline n-Si wafers (156 × 156 × 0.18 mm^3, 0.5–3 Ω cm specific resistance) were used for this work. The pyramid surface texture was produced by chemical etching in a solution of KOH (Sigma, reagent grade) on a mass production line of crystalline-Si solar cells in the Suzhou company of Canadian Solar Inc. Then, an n^+ emitter layer was fabricated on the electrode surface using thermal diffusion of $POCl_4$ at 1000 ^{0}C, which is good for the ohmic contact with metal catalyst. Moreover, a p^+ layer was fabricated on the rear surface using Al diffusion. Bottom electrodes were screen-printed onto the rear surface. After drying the screen-printed samples at 150 ^{0}C for 5 min to vaporize the organic solvents in the Al paste, an ohmic contact is formed in an infrared conveyor belt furnace at 900 ℃ for about 13 s. This n^+np^+-Si structure can boost the photovoltage by replacing the Si/liquid junction with a built-in p–n junction. We called such a photocathode n^+np^+-Si. For the convenience of the experiment, these Si wafers were cleaved into 1.5 × 1.5 cm pieces.

ELD of Pt:

Three $H_2PtCl_6 \bullet 6H_2O$ containing solutions are used: (1) WA-diluted 2 M HF and 1 mM $H_2PtCl_6 \bullet 6H_2O$; (2) ISO-diluted 2 M HF and 1 mM $H_2PtCl_6 \bullet 6H_2O$; and (3) ISO-diluted 2 M HF and 1 mM $H_2PtCl_6 \bullet 6H_2O$ plus 5% water. n^+np^+-Si substrates were firstly cleaned in alcohol-diluted 5% hydrofluoric acid (HF) for 30 seconds to remove the possible SiO_2 on Si surface. Then, the Si substrate was immersed into the above solutions, respectively. After some time of immersion, the substrate was taken out and rinsed in pure water, and dried in air.

Fabrication of TiO_2 protective layer:

Thin layers of amorphous TiO_2 were deposited onto the Si photocathode using a thermal ALD system (Ensure NanoTech, China). TiO_2 layers were deposited at a reaction chamber temperature of 150 ℃ using tetra(dimethylamino) titanium (TDMAT) (99.99%, Aldrich) and high-purity H_2O as the Ti and O precursors, respectively. TiO_2 layers were deposited in pulse mode under a nitrogen flow of 5 sccm and the growth rate was ~0.6 Å per cycle at 150 ℃. The thickness of the TiO_2 film can be regulated by controlling the cycle number. The number of ALD cycles was 250, and a film thickness of ~15 nm was measured using TEM.

Sample Characters:

PEC measurements were conducted in a three-electrode cell configuration, using the Si photocathode as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and a Pt wire as the counter electrode. The PEC experiments were performed using an electrochemical workstation (Vertex, Ivium Technologies) in a custom-built Teflon electrolytic cell, except for hydrogen quantification measurements. The rear of the Si photocathode is in contact with a spring-loaded Cu plunger which also presses the working electrode against a Teflon gasket. Thus only the active area (~0.5 cm^2) of the Si photocathode touches the electrolyte. The working electrode was illuminated through a fused silica window, using simulated AM1.5G illumination provided by a 300 W Xe lamp (Oriel, Newport Co.) with an AM1.5G filter (Zhao Jiu Photoelectric Technology Co., LTD). During the PEC measurement, the light intensity was carefully maintained at 100 mW/cm^2, measured using an optical power meter (Newport company) just before the light entered the PEC cell. All potentials were referenced to the RHE for convenience, according to the following equation: E(RHE) = E(Ag/AgCl) + 0.059V × pH, where E(Ag/AgCl)=0.197 V. The photocurrent *vs.* potential curves were measured at 50 mV s^{-1} in a solution containing 1 M $HClO_4$ (Sinopharm Chemical Reagent Co., Ltd., analytical reagent).

To measure the stability of the photoelectrode, potential *vs.* time measurements were conducted at a constant current density of -10 mA cm^2 for proton reduction in 1 M $HClO_4$ solution under simulated AM1.5G illumination. The electrolyte was replaced and the sample was rinsed every 24 h during the stability measurements. EIS was performed under a 100 mW/cm^2 Xe lamp illumination when the working electrode was biased at a constant potential of 0.5 V *vs.* RHE while sweeping the frequency from 300 kHz to 10 Hz with a 10 mV AC dither and modeled using an equivalent circuit.

SEM surface and cross-section images were observed with a Hitachi SU8010 field-emission SEM. Cross-sectional TEM analysis were performed by a Tecnai G220 (S-TWIN, FEI) operating at 200 kV.

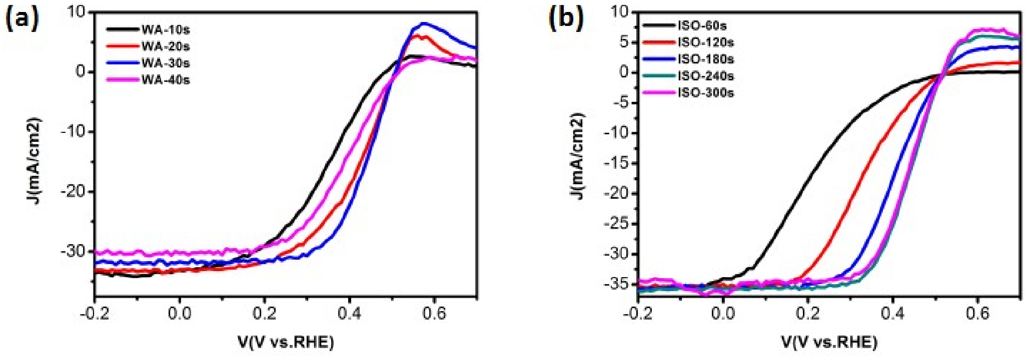

Fig. S1 (a) J-V curves of the WA/A-Si samples obtained under different immersion time (10s, 20s, 30s and 40s) in WA-diluted solution; (b) J-V curves of the ISO/A-Si at different immersion time (60s, 120s, 180s and 240s) in ISO-diluted solution plus 5% water.

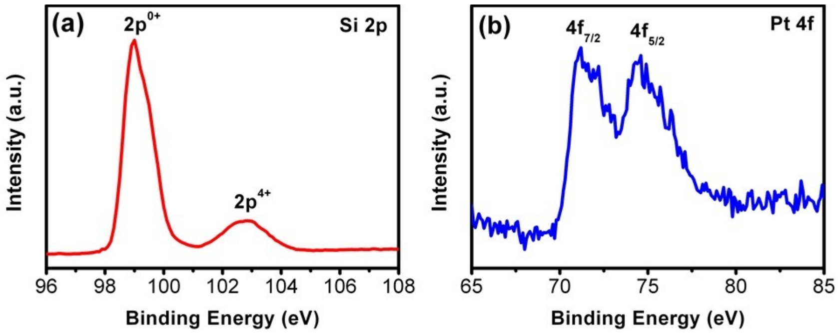

Fig. S2 High-resolution XPS (a) Si 2p and (b) Pt 4f spectra of the Pt/Si electrode.

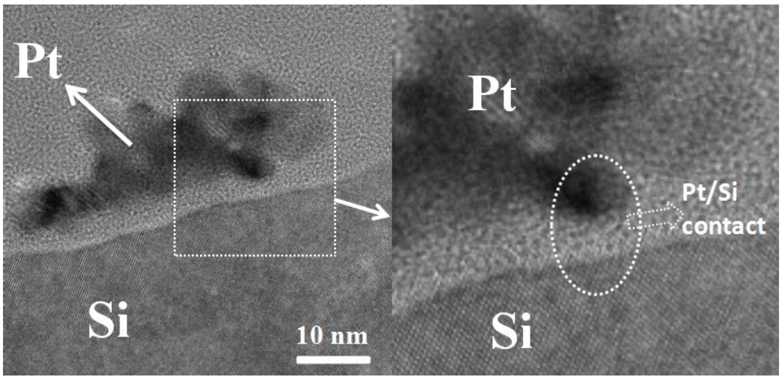

Fig. S3 TEM picture for the Pt/Si contact.

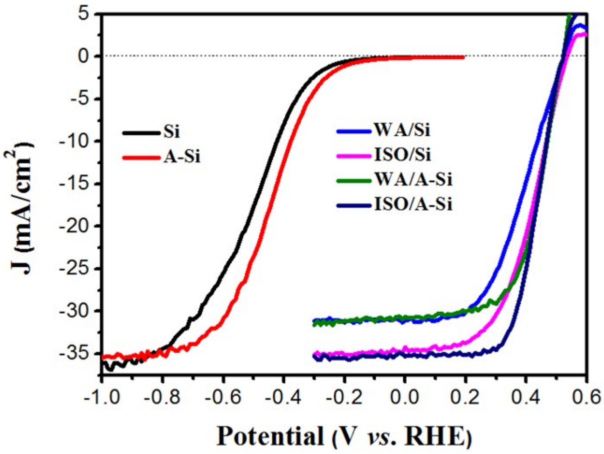

Fig. S4 J-V curves of the n$^+$p-Si (Si), annealed n$^+$p-Si in forming gas (A-Si), Pt/n$^+$p-Si where Pt is deposited in WA-diluted solution (WA/Si) or in ISO-diluted one (ISO/Si), WA/A-Si and ISO/A-Si photocathodes.

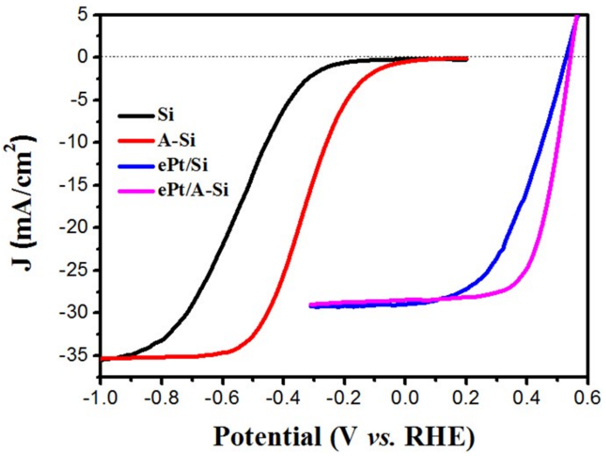

Fig. S5 J-V curves of the n^+np^+-Si (Si), annealed n^+np^+-Si in forming gas (A-Si), Pt/n^+np^+-Si where Pt is electro-deposited in $H_2PtCl_6{\bullet}6H_2O$ solutions (ePt/Si), and ePt/A-Si photocathodes.

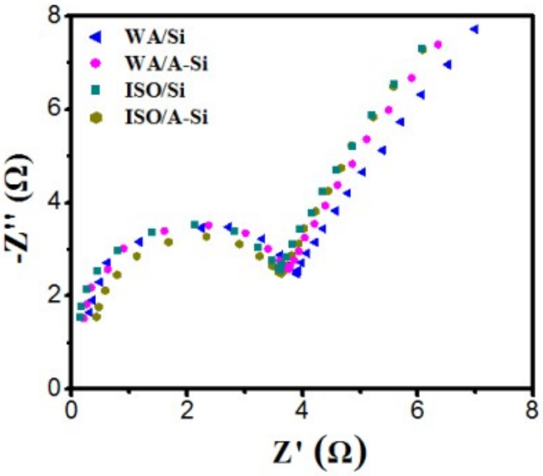

Fig. S6 Enlarged left semicircle of Fig. 3(a).

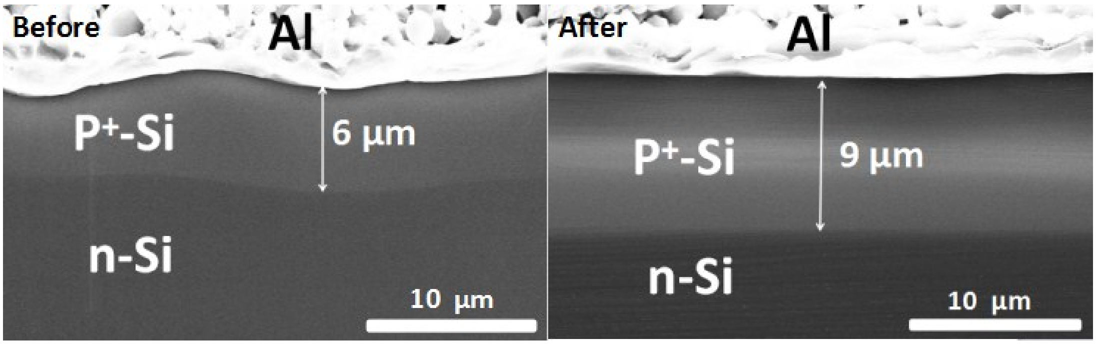

Fig. S7 Cross section SEM measurements for the interface of Al-p^+ Si back electrodes before and after the annealing in H_2/Ar.

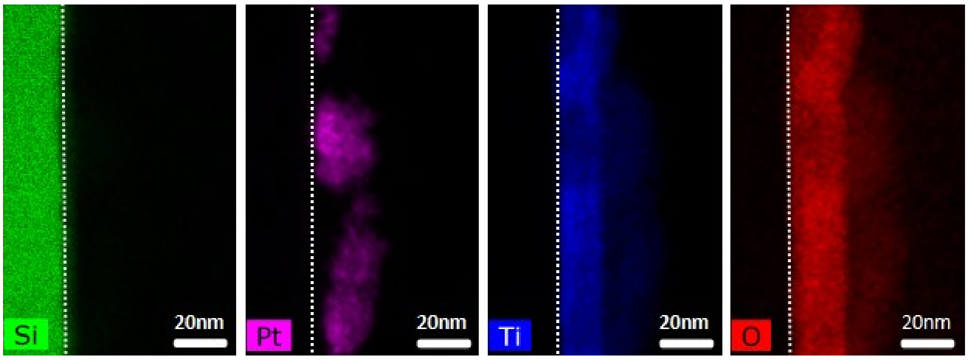

Fig. S8 STEM-EDS mappings for Si, Pt, Ti and O in TiO_2/ISO/A-Si photocathode.