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# **Supporting Information**

## **Engineering Interfacial Silicon Dioxide for Improved MIS Silicon Photoanode Water Splitting Performance**

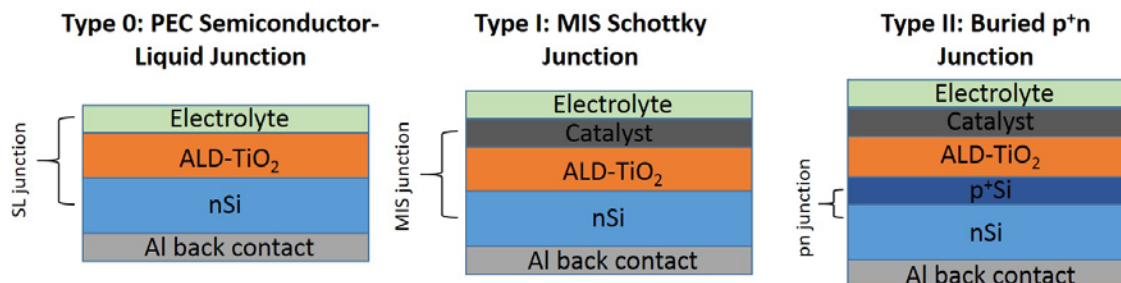
*Peter F. Satterthwaite<sup>a</sup>, Andrew G. Scheuermann<sup>a</sup>, Paul K. Hurley<sup>b</sup>, Christopher E. D.  
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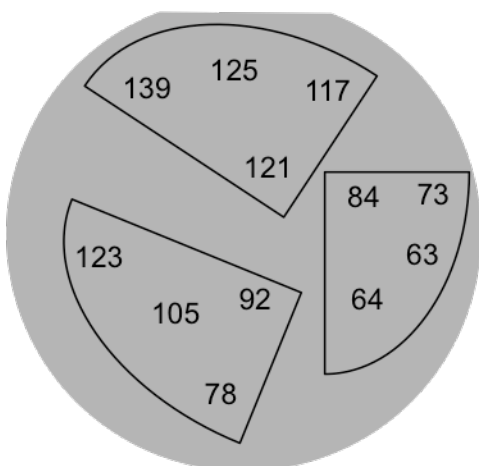
<sup>c</sup>Department of Chemistry, Stanford University, Stanford, CA, United States

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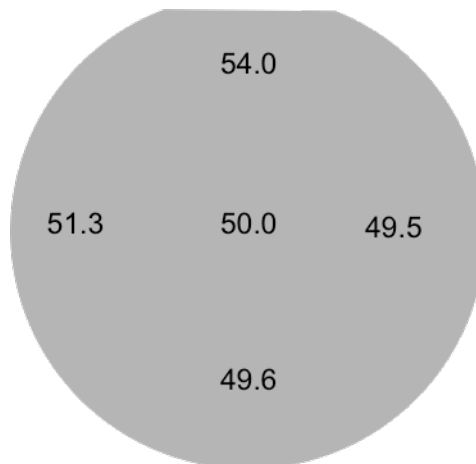


**Figure S1 | Photovoltaic-Based PEC Cell Types** The three types of junctions routinely utilized for photoelectrochemistry shown with the example of ALD-TiO<sub>2</sub> protection of silicon photoanodes. Type 0 photoelectrosynthetic cells<sup>1</sup> generate voltage from a semiconductor-liquid junction typically using a stable metal-oxide layer on the semiconductor substrate. Type 1 photovoltaic-biased photoelectrosynthetic cells<sup>1</sup> generate voltage from a metal—insulator-semiconductor (MIS) Schottky junction with an interposed protection layer. Type 2 photovoltaic-biased photoelectrosynthetic cells<sup>1</sup> generate voltage with a buried p<sup>+</sup>n junction with the metal oxide protection layer and catalyst in series. Type 2 photoanode cells are often realized by doping the top portion of an n-type substrate to create a thin p<sup>+</sup> region.

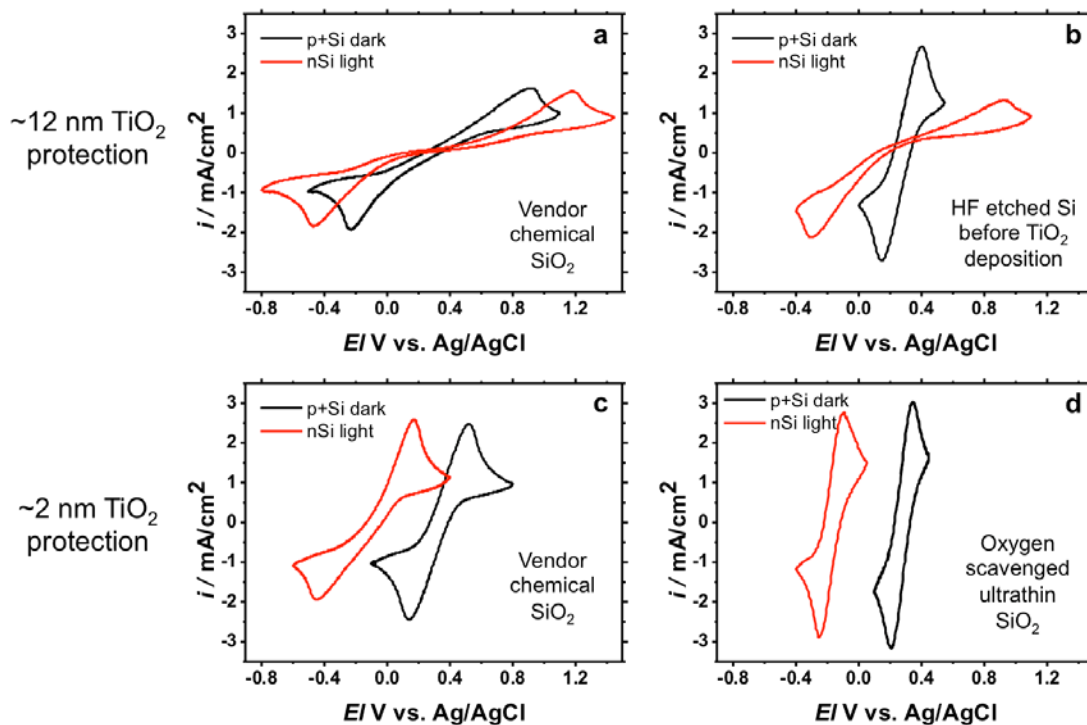
**a** HF Etched Wafers



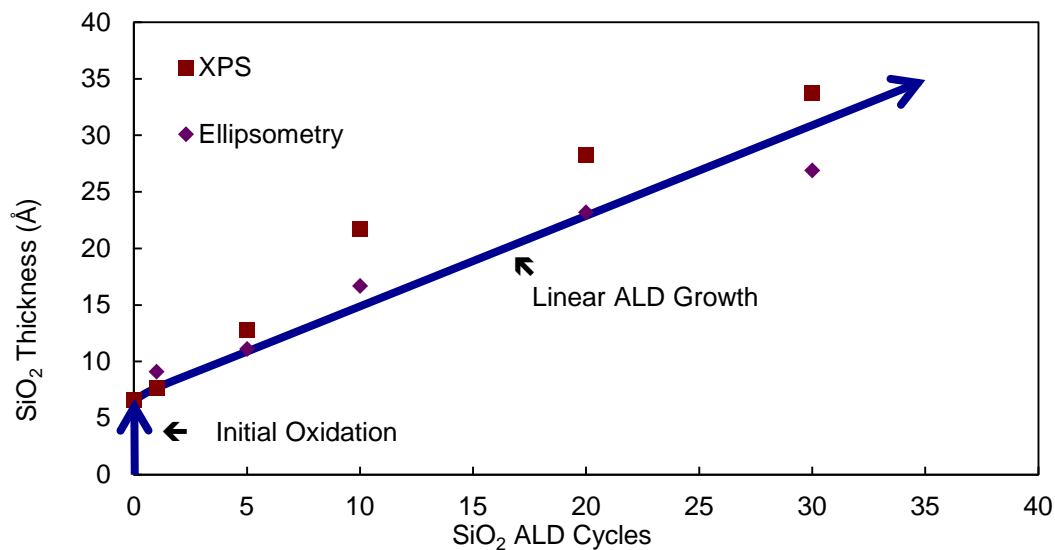
**b** Wafer with Native Oxide



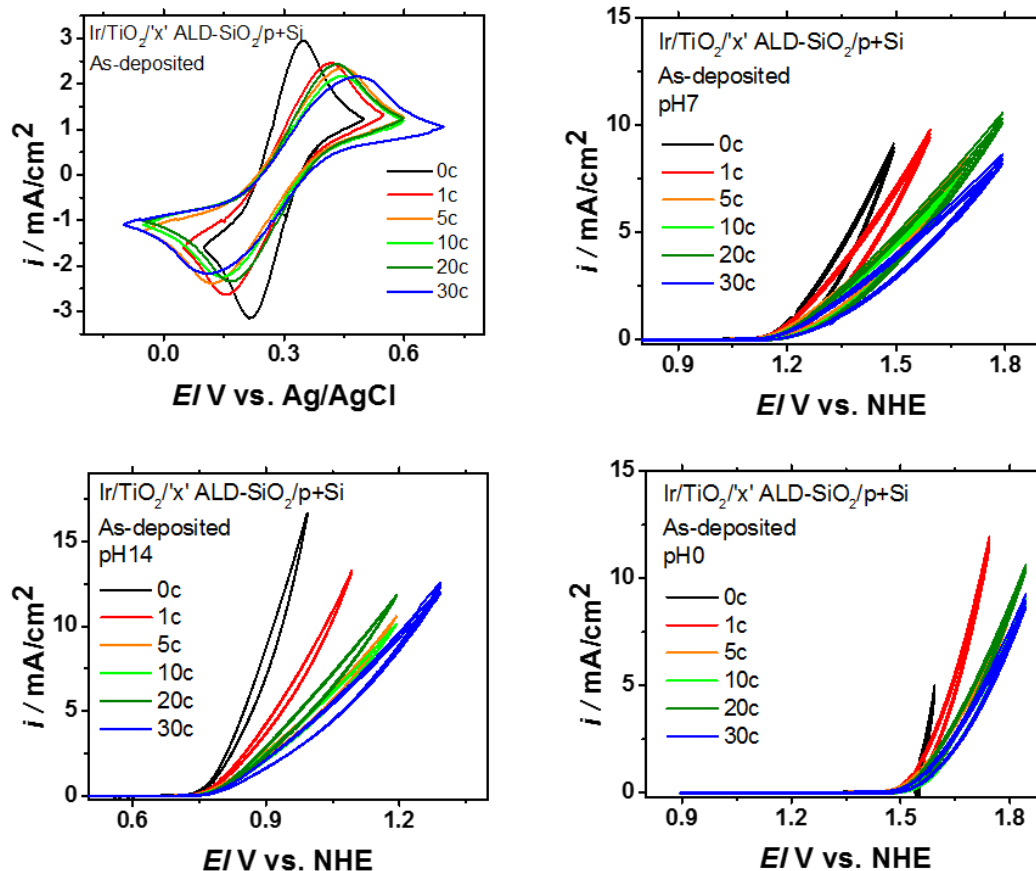
**Figure S2 | Thickness of TiO<sub>2</sub> deposition by ALD on an HF-last surface and vendor chemical oxide.** Deposition on HF last surface (**a**) shows much higher thickness variation than qualification run performed on the same silicon substrate with the chemical oxide in place (**b**) immediately after using the same chamber conditions on the vendor chemical oxide for a 100 cycle run.



**Figure S3 | Photovoltage comparisons for various 2 nm Ir/TiO<sub>2</sub>/SiO<sub>2</sub>/silicon anodes, with a range of thin SiO<sub>2</sub> configurations** which can be measured as the shift of the p<sup>+</sup>Si anodes measured in the dark (black trace) to the nSi photoanodes measured in 1 sun of AM 1.5G illumination (red trace). **(a)** ~12 nm TiO<sub>2</sub>/vendor chemical-oxide/Si showing the zero to negative photovoltage observed in these systems with moderately leaky TiO<sub>2</sub> **(b)** ~12 nm TiO<sub>2</sub>/HF-last Si showing much increased conductivity for the p<sup>+</sup>Si anode but a flattened nSi curve suggesting strong recombination limiting the anodic current. This is likely due to a poor quality interface with high trap density leading to increased trap-mediated recombination. **(c)** ~2 nm TiO<sub>2</sub>/vc-oxide/Si showing an ~500 mV photovoltage with moderately leaky TiO<sub>2</sub> giving some residual resistance stretching out the CV. **(d)** ~2 nm TiO<sub>2</sub>/scavenged vc-oxide/Si showing a strong photovoltage shift of 500-550 mV and near-ideal conductivity of both the dark anode and the illuminated Schottky junction nSi photoanode.

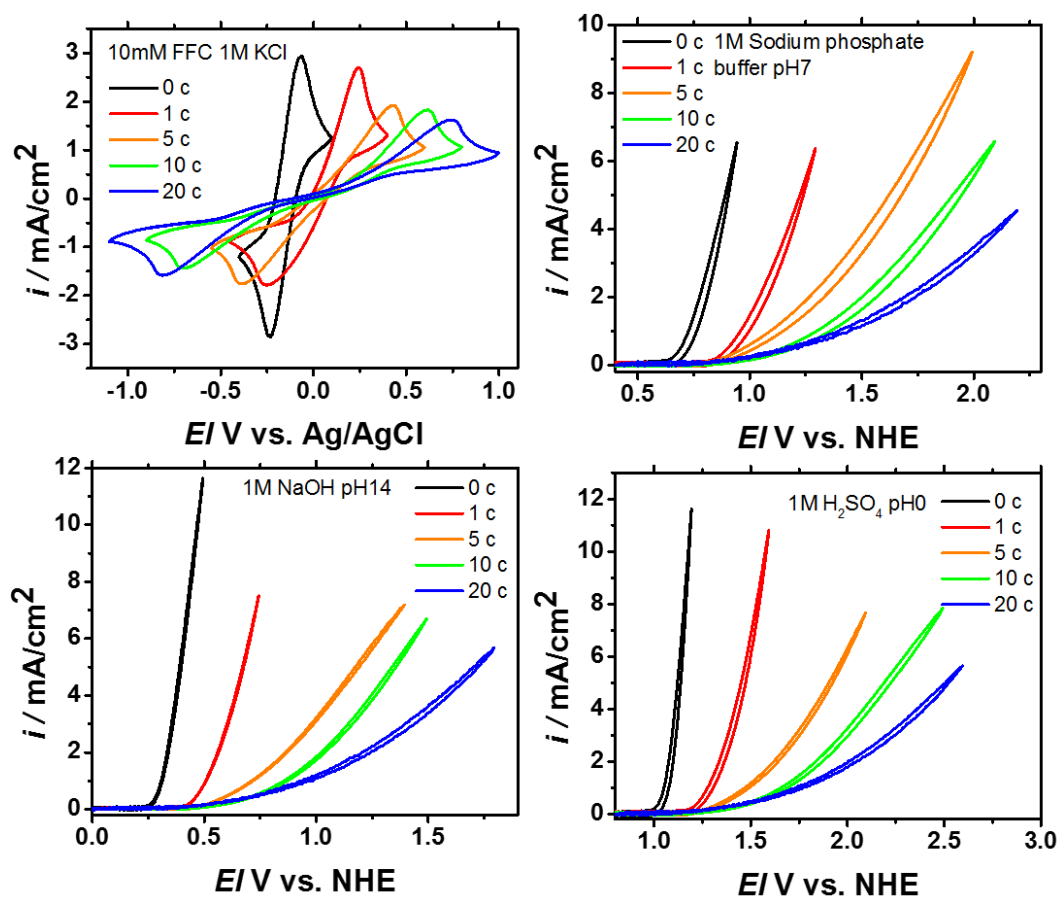


**Figure S4 | SiO<sub>2</sub> ALD thickness measured from XPS and ellipsometry.** The purple diamonds represent thicknesses characterized ellipsometrically. The red squares represent thickness characterization performed via XPS analysis and equation (1). The blue vertical line at zero ALD cycles of SiO<sub>2</sub>, represents initial oxidation of the HF-last surface, and subsequent linear ALD growth is  $\sim 0.8 \text{ Å/cycle}$ , as is typical for this process. The 0 cycle sample displays a non-zero SiO<sub>2</sub> thickness representing oxidation resulting during the TiO<sub>2</sub> ALD process on an HF-last surface as discussed in the manuscript.



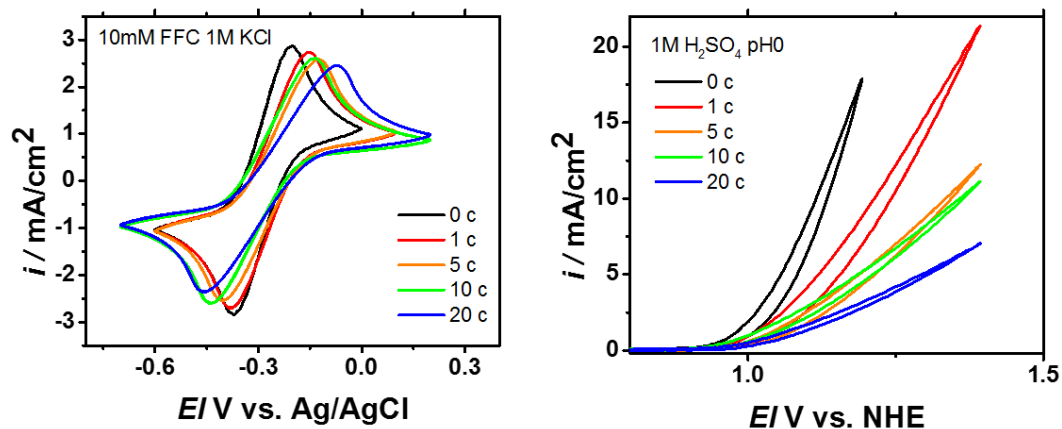
**Figure S5 | Ir / ~ 2 nm TiO<sub>2</sub> / 'x' cycles of ALD-SiO<sub>2</sub> / p<sup>+</sup>Si electrochemistry results.**

The results in ferri/ferrocyanide, pH 14 1M NaOH, pH 7 phosphate buffer, and pH 0 1M H<sub>2</sub>SO<sub>4</sub> are shown here demonstrating the slowly scaling increased turn-on overpotentials at 1mA/cm<sup>2</sup> shown in figure 5.



**Figure S6 | Ir / ~2 nm TiO<sub>2</sub> / 'x' cycles ALD-SiO<sub>2</sub> / nSi electrochemistry results.** The results in ferri/ferrocyanide, pH 14 1M NaOH, pH 7 phosphate buffer, and pH 0 1M H<sub>2</sub>SO<sub>4</sub> are shown here demonstrating the much more rapidly scaling overpotential loss as shown in Figure 5 (main paper) for the Schottky nSi photoanodes. Figure 4 (main paper) resistance modelling is performed from the ferri/ferrocyanide nSi profiles shown in the upper left quadrant.





**Figure S7 | Ir / ~2 nm TiO<sub>2</sub> / ‘x’ cycles ALD-SiO<sub>2</sub> / p<sup>+</sup>n Si electrochemistry results.**

The results in ferri/ferrocyanide and pH 0 1M H<sub>2</sub>SO<sub>4</sub> are shown here demonstrating the slowly scaling increased turn-on overpotentials for buried junction p<sup>+</sup>nSi photoanodes similar to the p<sup>+</sup>Si reference anodes where only an Ohmic resistance remains from the extra interlayer insulators as opposed to the photovoltage loss seen in Figure S6 by the nSi Schottky junction photoanodes.

## Supporting References

- (1) Nielander, A. C.; Shaner, M. R.; Papadantonakis, K. M.; Francis, S. A.; Lewis, N. S. A Taxonomy for Solar Fuels Generators. *Energy Environ. Sci.* **2015**, 8 (1), 16-25.