Effects of Catalyst Material and Atomic Layer Deposited TiO₂ Oxide Thickness on the Water Oxidation Performance of Metal-Insulator-Silicon Anodes

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Supporting Materials

Materials for thickness series. All chemicals used in this study were purchased from commercial sources and used as-received without further purification. The Si wafers used were degenerately doped p-type Si (100) wafers (p-Si, 0.001-0.002 Ω cm, 500 µm thickness) obtained from El-Cat. The wafers were used as-received, with a ~1.5 nm chemical SiO₂ layer, as prepared by the wafer vendor. The catalyst layer was formed by e-beam evaporation of 2 nm of Ir onto the ALD-TiO₂ layer. The backside contact was 20 nm of Pt deposited by e-beam evaporation which was used to avoid any Schottky Junctions that might form. The electrolyte solutions were made by dissolving the appropriate reagent into Millipore filtered water (10 M Ω resistance) obtained on a Millipore filtration system. A ferri/ferrocyanide (FFC) solution was made to be 10 mM of both K₃Fe(CN)₆ and K₄Fe(CN)₆·3H₂O in 1 M aqueous KCl. Experiments for water electrolysis were performed in either acidic (1 M H₂SO₄), neutral (1 M phosphate-buffered, pH 7) or basic (1 M NaOH) solutions. The pH of the neutral solution was made by dissolving Na₂HPO₄ and NaH₂PO₄ in water with the pH adjusted until a pH of 7 was achieved. All pH values were calculated by measuring the reversible hydrogen potential in each solution and all solution resistance measurements obtained by electrochemical impedance spectroscopy.

Materials for catalyst metal series. The metal deposition for different catalyst layers was performed by e-beam evaporation of all the catalyst layers used in this study, with the Co-Pi

system deposited according to published methods.¹ The rest is as above with two notable differences: The backside contact was just 2 nm; no difference in performance was observed in matching samples with 2 or 20nm backside contacts. Secondly, after fabrication, these samples were heated to 400° C for 30 minutes in a forming gas environment (95% N₂, 5% H₂).

Materials for MOSCAP analysis. MOS capacitors were fabricated on n-Si (100) wafers (n-Si, 0.13830-0.24310 Ω cm, 525 µm thickness) obtained from Okmetic Inc. These were also used as received, with ~1.5nm of chemical SiO₂ on the surface and without a forming gas anneal. Electrode films of 50 nm of Pt, 50 nm Ir, and 100 nm Al for the MOSCAP studies were deposited by e-beam evaporation while 50 nm Ni and 50 nm Pd were deposited by thermal evaporation. In all cases, a stencil was used to define circular diodes ranging from 100 to 250 µm in diameter. All results are reported measuring on the 100 µm capacitors. The backside contact was 100 nm of e-beam deposited Al to form avoid a Schottky barrier with n-Si.

Sample Preparation. Atomic layer deposition (ALD) of TiO₂ was performed at 170°C on silicon wafers that were coated with a thin chemical oxide as a result of surface preparation by the wafer vendor. Tetrakis-(dimethylamido)titanium (TDMAT) was used as the titanium source and water vapor as the oxygen source. Each reagent was heated to a line temperature of 80°C with the system pressure maintained at 0.6 Torr. For the thickness series, p+Si, p-Si, n-Si, and glass were deposited on simultaneously for every run. This allowed the measured overpotential on p+Si anodes to be matched directly to corresponding capacitance voltage and optical analysis for any given ALD run. Ellipsometry was performed after every run, while cross sectional TEM was only performed on four samples for calibration purposes.

Transmission Electron Microscopy for Thickness Calibration Cross-sectional TEM was conducted on four Ir/TiO₂/SiO₂/p+-Si samples with 2 nm, 5 nm, 8 nm, and 12 nm of TiO₂ to span the range studied, three of which are shown in the paper. The ellipsometer was calibrated using these results. TEM specimens were thinned down to electron transparent thicknesses (typically < 100 nm) using a combination of mechanical grinding and polishing steps, followed by an Ar ion milling with the ion energy of 5 keV. Prepared TEM samples were imaged in FEI Tecnai G2 F20 transmission electron microscope at Stanford Nanocharacterization Laboratory. Bright field imaging was conducted with the electron acceleration voltage of 200 kV.

Atomic Force Microscopy (AFM). AFM and conductive AFM (CAFM) were measured both in air and in vacuum showing a pinhole free surface. Images were acquired using a Park XE-100 in air and a Seiko Instruments SPI 3800N in vacuum of 10^{-6} Torr. In both cases, -10 mV was applied to the substrate keeping the tip grounded. This low voltage produced up to 24.2 nA of uniformly distributed current in vacuum as can be seen below in figure S1. In CAFM when working with insulators the measured current can be defined as the product of the current density and the area of the tip ~100 nm². In the present case, the anode has an iridium metal coating that will increase the sampled area due to lateral conduction. From previous work by Chen and Prange (supporting information),¹ 10mV applied to solid state anodes with an Ir/2nm TiO₂/SiO₂/p+Si structure resulted in a current density of approximately 20mA/cm², which would suggest an effective measured area of 121 μ m² given 24.2 nA of current and assuming this device and measurement were identical. The actual measured area is unlikely to be this large indicating an even larger current density. While studying the details of this phenomenon is beyond the scope of this work, it is believed that the chosen applied voltage, which produces a uniform current below saturation levels, accurately demonstrates a pinhole free surface.

Electrochemical Methods. All electrochemical experiments were performed on a WaveNow potentiostat (Pine Research Instrumentation) in air at room temperature. A Pt wire was used as the counter electrode and a glass frit-isolated Ag/AgCl/sat. KCl electrode as the reference electrode. A 5 mm bored Teflon cone (area 0.196 cm²) was pressed against the catalyst/TiO₂/p-Si sample that was used as the working electrode. The pH values for the electrolyte solutions used in this study were determined by utilizing a reversible hydrogen electrode (RHE) and measuring the open circuit potential for each solution and adjusting the water oxidation potentials accordingly. RHE measurements were conducted by sparging hydrogen gas into the electrolyte solutions for ten minutes, with a platinum rotating disc electrode used as the working electrode and platinum mesh as the counter electrode. All measured potentials in this study were collected using the Ag/AgCl reference electrode and then converting to the NHE reference scale using E(NHE) = E(Ag/AgCl/KCl) + 0.197 V. All cyclic voltammograms (CVs) were measured at 100 mV/s in the indicated electrolyte solution. A peristaltic pump (Cole Parmer, Norprene tubing, ID = 1.6 mm) was used to continuously circulate electrolyte solution at a flow rate of ~1 mL/s impinging on the sample in the bore of the Teflon cone for all dark water electrolysis experiments.

Impedance spectroscopy measurements. Impedance spectroscopy was performed on a Princeton Applied Science impedance spectrometer to determine the solution resistance of the electrolytes used in this study. Extrapolation of the Nyquist plots to large frequencies reveals series resistance to be 4.3 Ω , 11.2 Ω , 40.0 Ω , and 18.4 Ω for the acidic, neutral, basic, and FFC solutions, respectively. Only the water splitting results were corrected for this series resistance as reported in the manuscript. The ferri/ferrocyanide series resistance was subtracted out only for modelling the resistance change in these voltammagrams as shown in figure S6 below.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed to characterize the different metal catalyst results using a PHI VersaProbe system with a 100 W Al-K α X-ray source on a spot size of 100 μ m at a 45° incident angle. The binding energy scan range was 0-1000 eV in 1 eV steps with a pass energy of 117.4 eV for survey scans. High resolution scans were taken in the appropriate ranges for each atom in 0.1 eV steps with a pass energy of 23.1 eV. A dual beam neutralizer (7 V Ar⁺ and 30 V electron beam) was used to neutralize sample charging. The result for Ru is presented below (Figure S2.C).

Platinum Catalyst Layer. The Pt catalyst layer was deposited onto the TiO_2/p -Si anode by physical vapor deposition methods and found to be 2 nm thick. Cyclic voltammograms for the Pt coated sample in the FFC solution and 1 M H₂SO₄, 1 M phosphate buffered and 1 M NaOH solutions are shown in Figure S1A and S1B.

Ruthenium Catalyst Layer. The Ru catalyst layer was deposited onto the $TiO_2/p+Si$ anode via e-beam physical vapor deposition. The thickness was found to be 3 nm. The cyclic voltammogram of the Ru layer in the FFC solution shows normal behavior for a catalyst that allows for facile charge transport through the structure (Figure S2A). For water oxidation, however, the Ru on the first CV cycle was found to have an irreversible oxidation peak before onset of water oxidation (Figure S2B). On the second cycle, the pre-water oxidation peak was not observed, and the water oxidation efficiency was measured. With each successive cycle, the water oxidation peak was found to decrease until ultimately the peak became too small to measure at 1 mA/cm² current density. The Ru sample was analyzed by XPS after analysis and was found to have a sharp decrease in the amount of Ru on the surface when compared to the freshly prepared portion of the sample (Figure S2C).

Cobalt Catalyst Layer. The Co catalyst layer was deposited by e-beam physical vapor deposition and found to be 2 nm thick. Curiously, CVs performed in the FFC solution yielded no peaks in the potential windows scanned. Activity for water oxidation on this catalyst was found to be sluggish requiring greater overpotentials to reach 1 mA/cm² (Figure S3A). We then decided to deposit the CoPi water oxidation catalyst onto this Co catalyst layer to see if the water oxidation performance improved. After performing chronoamperometry at 1.29 V for up to 3 hours from a 0.5 mM CoSO₄ solution in 100 mM phosphate buffered solution, the current measured reached a maximum and the CA was stopped and the deposition solution was removed and replace with each a 1 M H₂SO₄, 1 M phosphate buffered and 1 M NaOH solution. The water oxidation overpotential was decreased dramatically in the neutral solution (Figure S3B). However, the water oxidation behavior in both acid and base seemed to have negligible effect with the CoPi catalyst deposited.

Gold Catalyst Layer. A 2 nm thick layer of gold was deposited by physical vapor deposition methods. The layer was found to have large peak-to-peak splitting for the FFC solution (Figure S4A) and a large overpotential for the basic solution water oxidation (Figure S4B). The benchmark current density value of 1 mA/cm² was never obtained in the acidic or neutral solutions.

Modeled FFC Cyclic Voltammagrams. The cyclic voltammograms obtained in ferri/ferrocyanide were fit to theoretically determined profiles using EC-lab software V10.21. The high-frequency impedance determined series resistance of 18.4 Ω was first subtracted from all the data (only for this analysis, not subtracted for figures 3 or 5 in the paper). The best performing anode with 1.2 nm of ALD-TiO₂ was then fit assuming no uncompensated series resistance, a surface area of 0.196 cm², catholyte and anolyte concentrations of 10mM, a scan

rate of 100mV/s, room temperature, and the charge transfer coefficient α =0.50. The best fit was obtained with E₀ =0.29 vs Ag/AgCl/sat. KCl electrode, k₀ = 0.01 cm/s, D₀ = 8.5 x 10⁻⁶ cm²/s, and D_R = 3.5 x 10⁻⁶ cm²/s (S6A). Comparing these fitted parameters to literature: Daum and Enke find that the rate on an oxidized Pt electrode is 0.028, ten times less than the reduced surface.³ It is not unreasonable to think a similar rate constant would apply to iridium oxide. Konopka and McDuffie studied the FFC redox couple also finding a higher diffusivity of the reduced species, in particular D₀=7.3 x 10⁻⁶ cm²/s and D_R = 6.7 x 10⁻⁶ cm²/s.⁴ The voltammogram of each anode with increasing TiO₂ thickness in ferri/ferrocyanide was then fit with the same parameters, only varying the uncompensated series resistance. Figure S6B shows the slope of this resistance times the surface area as a function of TiO₂ thickness. The slope is again linear 10 Ω •cm²/nm with high correlation, R²=0.92, and is plotted on the same graph as the 23 mV/nm trend of the half peak-to-peak splitting of the ferri/ferrocyanide hysteresis. Because the peak current is around 2 mA/cm², these slopes roughly correspond to a TiO₂ resistivity of 1-2 x 10⁸ Ω •cm as compared to 2 x 10⁸ Ω •cm predicted from the water oxidation overpotential analysis reported in this paper.



Figure S1. (A) AFM and (B) c-AFM taken in vacuum 10^{-6} Torr applying 0V (first lines from the top) and -0.01V (rest of the scan) to the substrate while keeping the tip grounded. These images reveal a pinhole-free surface without any spikes in electrical conductivity that could indicate shorts through the protective ALD-TiO₂ coating.



Figure S2. (A) CV with 2 nm of Pt on $TiO_2/p+Si$ in the FFC solution. (B) Water oxidation CVs for Pt sample in acidic, neutral and basic solutions. The reduction wave in the acidic solution is attributed to the reduction of a Pt-O layer formed during water oxidation.



Figure S3. (A) CV with 3 nm Ru deposited onto $TiO_2/p+Si$ in the FFC solution showing oxidation and reduction peaks. (B) Water oxidation CVs in 1 M Acid (—) and 1 M phosphate buffered (—) solutions showing the decreasing current density with increasing cycle number, indicating that the Ru catalyst is coming off the surface. (C) XPS narrow scans in the Ru region showing the amount of Ru on the electrode after preparation is much greater than the amount of Ru on the electrode after analysis.



Figure S4. (A) Water oxidation CVs in acidic (—), neutral (—) and basic (—) solutions for a 2 nm Co catalyst layer deposited onto 2 nm $TiO_2/p+Si$. (B) Water oxidation CVs of the Co layer from (A) with the CoPi catalyst deposited *in situ*.



Figure S5. (A) CV of 2 nm of gold deposited onto 2 nm of $TiO_2/p+Si$ in FFC solution. The peak-to-peak splitting is considerably wider than other deposited catalyst layers, possibly due to poor adhesion of the gold to the TiO_2 layer. (B) CVs of the gold sample in basic (—) and neutral (—) solution for water oxidation. The results show that the obtained current density is considerably lower than for other water oxidation catalysts as well as a loss of the gold layer as a function of cycle number.



Figure S6. (A) CV of (—) 2nm Ir/1.2nm TiO₂/1.5nm SiO₂/p+Si in FFC solution compared to (--) a simulated fit using EC-lab software. (B) The (—) 23 mV/nm dependence of the half peak-to-peak splitting compared with the (—)10 Ω •cm²/nm trend of the modeled uncompensated series resistance. The results are linear in both cases and predict a TiO₂ resistivity of 1-2 x 10⁸ Ω •cm.

Supporting References

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