Supporting Information for:

Atomic Layer Stack Deposition-Annealing Synthesis of CuWO₄

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Experimental

Film Deposition. Atomic layer deposition was performed using a Savannah 100 reactor (Cambridge Nanotech Inc.) at a temperature of 250 °C. Fluorine-doped tin oxide (FTO) coated glass (Hartford Glass, TEC 15, 12Ω cm⁻²), Si wafer (University Wafer) and quartz (Technical Glass Products, 1/16 inch thick) were used as the substrates. The substrates were sonicated in soap water, distilled water and isopropanol, and blown dry with nitrogen prior to deposition. The precursors for the deposition of WO₃ and CuO were bis(tert-butylimido)bis(dimethylamido) tungsten (VI) ((^tBuN)₂(Me₂N)₂W) (Strem Chemicals Inc., >97%) and Copper(I)-N,N'-di-secbutylacetamidinate ([Cu(^sBu-amd)]₂) (Dow Chemical Co., >99.0%), respectively. The nitrogen carrier gas was kept at 5 sccm. WO₃ was deposited using a modified version of a reported procedure.¹ The precursor was heated up to 75 °C but the vapor pressure was too small to be detected by our pressure gauge. In each ALD cycle, the tungsten precursor was pulsed for 2 s, followed by 10 s under exposure mode and 6 s nitrogen purge. De-ionized water (millipore, 18 M Ω m) was used as the oxidant and was pulsed for 0.5 s followed by 15 s of exposure mode and 6 s of purge. 2000 cycles of WO₃ (~160 nm) was deposited for characterization. The CuO was deposited using a modified recipe suggested by Ultratech Inc. (unpublished). The precursor was heated to 150 °C but the vapor pressure was not detectable by the pressure gauge. The Copper precursor was pulsed for 3 s in each ALD cycle. After purging for 6 s, the oxidation was performed. The oxidation was a 2 s ozone (~10% by weight O_3 in ultrahigh purity O_2 produced by Yanco Industries ozone generator) pulse, followed by a 3 s purge to allow for enough generation of ozone, and performed for 10 times. A total of ~1500 cycles of CuO (~150 nm) was deposited for the ease of characterization. These binary oxide films were sintered at 550 °C at a ramping rate of 10 °C/min and heated for 2 h. CuWO₄ thin films were made by depositing suitable cycles of CuO on top of WO₃ followed by annealing at 600 °C in air for 30 min at a ramping rate of 2 °C/min.

Film Characterization. The as-deposited and annealed films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. XRD was taken with Bruker Davinci Diffractometer operating at 40 kV and 40 mA using Cu Kα radiation. XPS analysis was made using Perkin Elmer Phi 5600 ESCA system with a magnesium Kα X-ray source at a takeoff angle of 45°. Survey scans of 0-1100 eV binding energy and detailed scans for C 1s, O 1s, W 4f and/or Cu 2p regions were scanned for all samples. Peaks were corrected with the C 1s peak set to 284.8 eV, and subsequent Shirley background subtraction was performed for fitting. Raman spectra were recorded using LabRam Armis, Horiba Jobin Yvon instrument equipped with 532 nm laser and a ×50 microscope to focus the laser on the film surface. The thicknesses of binary oxide films were obtained by ellipsometric measurements (Horiba Jobin Yvon, Smart-SE). Thickness of the ternary film and the surface morphology of the films were examined by atomic force microscopy (AFM) using MFP-3D from Asylum Research. Cross-section scanning electron microscopy (SEM) (Carl Zeiss Microscopy) was also used to determine the film thicknesses, as well as their morphology. Energy-dispersive X-ray (EDX) analysis spectra were collected using Ametek-EDAX Apollo X. Accelarating voltages used were 15 kV and 20 kV, with 8 mm working distance. Spectra were analyzed using TEAM EDS software. Cu K and W M emission lines were analyzed for 15 kV beam voltage and Cu K and W L were analyzed for 20 kV beam voltage. The error bar in the main text is the standard deviation of measurements on 10 different spots. Absorbance measurements were made using a Perkin-Elmer Lambda 35 UV-vis spectrometer with a Labsphere integrating sphere.

Photoelectrochemistry. Thin film electrodes were masked with a 60 μ m Surlyn film (Solaronix) with a 0.28 cm² hole to define the active area and to prevent scratching of the thin films which were clamped to a custom-made glass electrochemical cell. Surlyn films were adhered to the electrodes by heating to 120 °C. A homemade saturated Ag/AgCl electrode was used as a reference electrode, and high surface area platinum mesh was used as the counter electrode. All experiments shown used a pH 9 potassium borate (KBi) buffer containing 0.2 M KCl as a supporting electrolyte. The buffer was prepared by adding an appropriate amount of KOH pellets into 0.1 M H₃BO₃ to adjust the pH. The pH was determined using a Fisher Scientific Accumet pH meter. All photoelectrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. The light source was a 450 W Xe arc lamp. An AM 1.5 solar filter (Sciencetech Inc.) was used to simulate sunlight at 100 mW cm⁻² (1 sun). The *J-V* curves were measured at a scan rate of 20 mV/s by shining light from the electrolyte-electrode (EE, front illumination) interface. The monochromatic photocurrents (IPCE) were measured at 1.23 V vs RHE using the same light source coupled with a grating monochromator with a 10 nm step.



Figure S1. Thickness of WO₃ thin films vs number of deposition cycles using different metal precursor pulse lengths. ALD of WO₃ reaches saturation when the metal precursor pulse length is 2 s with a growth rate of 0.86 ± 0.03 Å/cycle. The growth rate is the average growth rate of four batches, including two batches pulsing 2 s and two batches pulsing 3 s. The error is calculated as the standard deviation of the four batches described above.



Figure S2. Experimental X-ray photoelectron spectroscopy (XPS) spectra of W 4f and O 1s peaks (black scatters) with fitting (red solid lines and dots) of as-deposited (top) and annealed (bottom) WO₃. The as-deposited film and annealed film both show W $4f_{7/2}$ and W $4f_{5/2}$ peaks at 35.6 eV and 37.8 eV, consistent with W⁶⁺ peaks in literature.^{2–5} The O 1s peak shows a main peak at 530.4 eV, corresponding to the metal oxide O 1s peak, with a small contribution from carbon bonded oxygen at 531.9 eV.



Figure S3. X-ray diffraction (XRD) patterns of as-deposited (black) and annealed (red) WO₃.



Figure S4. Raman spectra of as-deposited (black) and annealed (red) WO₃.



Figure S5. (a) XRD pattern and (b) Raman spectrum of FTO coated glass.

According to the XRD and Raman spectra in Figure S3 and S4, and compared with XRD and Raman spectra of FTO substrate (Figure S5), the as-deposited films appear to be amorphous since no peaks corresponding to WO₃ are present. After annealing, however, diffraction peaks at 23.0° , 24.3° and 34.1° clearly show the presence of WO₃. These peaks were assigned using the International Union of Crystallography (IUCr) database. Raman peaks at 272, 325, 713 and 808 cm⁻¹ also appeared with annealing, in agreement with Raman scattering from WO₃.^{6,7}



Figure S6. Thickness vs number of deposition cycles of CuO thin films with different metal precursor pulse length. The saturation growth rate with 1 s Cu source pulse length is 0.45 ± 0.04 Å/cycle, and 3 s pulse length was used in following experiments just to be conservative. This growth rate was calculated using the slope of the best fit line of the thickness vs number of cycles plot, but due to the surface-enhanced behavior^{8,9} of CuO on Si substrate, the intercept with the thickness axis is not zero. Thus, this growth rate in not reflecting the real growth rate of CuO on itself or in our case, on WO₃. This experiment is only to show the self-limiting growth behavior of CuO. In the following demonstration of ALD of CuWO₄, we are using the growth rate of CuO on WO₃ for calculation.



Figure S7. Experimental XPS spectra of Cu 2p and O 1s peaks (black scatters) with fitting (red solid lines and dots) of as-deposited (top) and annealed (bottom) CuO. The as-deposited film and annealed film both show Cu^{2+} peaks in the Cu 2p region. Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks are located at 933.9 and 953.8 eV, with their satellite peaks at 940.9, 943.4 (Cu $2p_{3/2}$ satellite) and 962.0 eV (Cu $2p_{1/2}$ satellite), respectively, which is the distinguishing feature of the XPS spectra of Cu²⁺.^{10,11} The O 1s peak shows a main lattice oxide peak at 529.8 eV and a small contribution from carbon bonded oxygen at 532.1 eV. Also, there is a huge deconvoluted peak at 531.2 eV, which can be attributed to the defective oxygen CuO.¹²



Figure S8. XRD patterns of as-deposited (black) and annealed (red) CuO.



Figure S9. Raman spectra of as-deposited (black) and annealed (red) CuO.

The XRD pattern and Raman Spectra of CuO films are shown in Figure S8 and S9. Both asdeposited and annealed CuO thin films are crystalline. All X-ray diffraction peaks agree with CuO diffractions according to the IUCr database, including CuO single crystals grown by different methods such as flux method^{13,14} and thermal decomposition of gerhardtite.¹⁵ Raman spectra show three peaks which are all assigned to Raman scattering of CuO.^{16–18}



Figure S10. Cross-section SEM images of (a) as-deposited WO_3 and (b) annealed $CuWO_4$ thin films on Si substrate.



Figure S11. AFM surface morphology image of (a) as-deposited WO₃, (b) as-deposited CuO on WO₃, and (c) annealed CuWO₄ on Si substrate.

The annealed $CuWO_4$ film has an RMS roughness of 4 nm. Comparing this value with the roughness of as-deposited WO₃ and as-deposited CuO on WO₃, which is 0.4 nm and 3 nm, respectively, we concluded that while the annealing process resulted in a slight increase in the roughness of our films, the resulted CuWO₄ film is overall smooth.



Figure S12. An example of an EDX spectrum using an accelerating voltage of 20 kV of CuWO₄ on FTO-coated glass.

An additional measurement with a 15 kV beam voltage was used to minimize the contribution from the underlying substrate, and the determined W:Cu ratio is 0.99 ± 0.02 .



Figure S13. Images of CuWO₄ thin films deposited on FTO substrates with 0, 500, 1000, 1500, 2000, and 2500 ALD cycles of WO₃.



Figure S14. Thickness of CuWO₄ films with different deposition cycles of WO₃ measured with AFM. Error bars represent the standard deviation of 10 different measurements on each film. The thicknesses of resulted CuWO₄ films show a linear relationship (red dash) with ALD cycles of WO₃, with a growth rate of 0.85 Å of CuWO₄/cycle of WO₃.



Figure S15. Top: (a) Absorbance of CuWO₄ thin films with ALD cycles of WO₃ of 500 (red solid), 1000 (orange dash), 1500 (yellow short dash), 2000 (green dash dot), and 2500 (blue dot). Bottom: Absorbance of CuWO₄ thin films at wavelength of (b) 400 nm and (c) 450 nm varying with different ALD cycles of WO₃. Error bars represent standard deviation of independent measurements on three different spots for each thickness.

These CuWO₄ thin films were deposited on FTO substrates. The absorption measurement was measured from the substrate side. The absorbance was calculated by correcting for the reflectance from the substrate using previously reported method.¹⁹ Figure S15a shows that the absorbance increases with increasing deposition cycles, in agreement with the trend of color shown in Figure S13. Figure S15b and c indicate a linear trend of absorbance of CuWO₄ at 400 nm and 450 nm with ALD cycles, confirming the consistent growth rate of CuWO₄ using our SDA method. Considering the thicknesses of these films shown in Figure S14, the absorption coefficients of CuWO₄ at 400 nm and 450 nm are calculated to be 58370 cm⁻¹ and 29058 cm⁻¹, respectively. These values are higher than most reported values,^{20–22} and close to those measured with cosputtered films (~20000 cm⁻¹ at 450 nm).²³ The differences may be due to differences in film density or methods used to correctly account for reflectance in absorption measurements.



Figure S16. XPS survey spectra of as-deposited (bottom) and annealed (top) film of CuO on top of WO_3 .



Figure S17. Experimental XPS spectra of (a) Cu 2p and W 4f peaks (black scatters) with fitting (red solid lines and dots) of CuO on top of WO₃ as-deposited (top) and annealed (CuWO₄) (bottom) and O 1s peaks (black scatters) with fitting (red solid lines and dots) of CuO on top of WO₃ (b) as-deposited and (c) annealed (CuWO₄).

Figure S17b-c shows the O 1s peaks of the as-deposited and annealed films, respectively, and both of them are fitted with three peaks. The peaks at 530.1 eV belong to the main lattice oxide peak. The peaks at 532.0 and 531.2 eV of as-deposited and annealed films are assigned to the defective oxygen.¹² Finally, the peaks at 533.2 and 532.2 eV in the as-deposited and annealed films are attributed to carbon-bonded oxygen.



Figure S18. *J-V* curve of (a) CuO and (b) WO_3 electrode in the dark (black) and under 1 sun illumination (red) measured in 0.2 M KCl in pH9 KBi buffer.



Figure S19. (a) IPCE (red scatters) in pH9 KBi buffer at 1.23 V vs RHE and absorptance spectrum (black solid line), (b) Tauc plot, and (c) absorption coefficient of CuWO₄ thin film.

Equation used to calculate the thickness of CuO needed to produce desired 1:1 stoichiometry with WO₃:

$$\frac{\rho_{WO_3} \times Area \times t_{WO_3}}{M_{WO_3}} = \frac{\rho_{CuO} \times Area \times t_{CuO}}{M_{CuO}}$$

$$t_{CuO} = t_{WO_3} \times \frac{\rho_{WO_3}}{\rho_{CuO}} \times \frac{M_{CuO}}{M_{WO_3}}$$

where n_{WO_3} , t_{WO_3} , ρ_{WO_3} and M_{WO_3} are the number of moles, thickness, density and molar mass of WO₃ (density 7.16 g/cm³, molar mass 231.84 g/mol), and n_{CuO} , t_{CuO} , ρ_{CuO} and M_{CuO} are the corresponding parameters of CuO (density 6.315 g/cm³, molar mass 79.545 g/mol). Since they are uniformly deposited on the same substrate, the area should be the same for both WO₃ and CuO. Thickness of WO₃ is measured by spectroscopic ellipsometry, and thus the thickness of CuO needed can be calculated.

Calculation of theoretical thickness of CuWO₄:

$$m_{WO_{3}} + m_{CuO} = m_{CuWO_{4}}$$

$$\rho_{WO_{3}} \times V_{WO_{3}} + \rho_{CuO} \times V_{CuO} = \rho_{CuWO_{4}} \times V_{CuWO_{4}}$$

$$\rho_{WO_{3}} \times A \times t_{WO_{3}} + \rho_{CuO} \times A \times t_{CuO} = \rho_{CuWO_{4}} \times A \times t_{CuWO_{4}}$$

$$\rho_{WO_{3}} \times t_{WO_{3}} + \rho_{CuO} \times t_{CuO} = \rho_{CuWO_{4}} \times t_{CuWO_{4}}$$

$$t_{CuWO_{4}} = \frac{\rho_{WO_{3}} \times t_{WO_{3}} + \rho_{CuO} \times t_{CuO}}{\rho_{CuWO_{4}}}$$

 ρ_{CuWO_4} and t_{CuWO_4} are the density and theoretical thickness of resulted CuWO_4. The density of CuWO_4 we used herein is 7.790 g cm⁻³, obtained by theoretical calculations based on the crystal structure in literature,²⁴ which is close to experimental values.^{24,25}

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