Supporting Information

Gas Phase Electrodeposition: A Programmable Multimaterial Deposition Method for Combinatorial Nanostructured Device Discovery

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Materials and Methods

Substrates for programmable deposition: A 500 µm thick p-type silicon wafer (Ultrasil) was first cleaned in a sulfuric acid and hydrogen peroxide solution at 115 °C for 15 min. Liquid phase chemical vapor deposition (LPCVD) was used to coat the surface with 500 nm silicon nitride. Photoresist (Microposit S1805) was spin coated at 3,000 rpm for 40s. After soft-bake at 105 °C for 1 min, the substrate was patterned with the 96 mJ/cm^2 UV light and developed in a developer (Microposit 351:H_2O= 1:5) for 25s and further cleaned using a 15s oxygen plasma. 20 nm Cr and 80 nm Cu were deposited by e-beam evaporation. Liftoff in acetone yields 1 µm wide and 2 mm long conducting lines that act as domain electrodes. Photolithography was repeated using the same conditions to apply an electrically insulating photoresist layer with localized openings to the underlying domain electrodes (figure 2).

Substrates to testing different photovoltaic cells architectures: The solar cell substrate was prepared using 10Ω per square indium-tin oxide (ITO) (Delta Technologies, LTD). After the ITO surface was cleaned using acetone, isopropanol, and distilled water in an ultrasonic bath, Photoresist (Microposit S1805) was applied by spin coating at 3000 rpm for 40s and exposed with the 96 mJ/cm^2 UV light. A 25s developing step was done in a developer (Microposit 351:H_2O= 1:5) and subsequently the substrate was wet-etched in Aqua Regia (HCl: HNO_3: H_2O= 3:1:4) to form five 500 µm wide and 2 cm long ITO strips. The patterned ITO was subsequently cleaned using acetone, isopropanol, and distilled water in an ultrasonic bath. Photolithography was repeated using the same conditions to apply an electrically-insulating photoresist layer with localized openings to the underlying strip-patterned ITO domains. Results are depicted in figure 3.

Postprocessing and characterization of the cell domains: Following localized deposition in the different domains to produce the desired nanostructured 3D nanowire electrodes an oxygen plasma was used for 30 min to remove the photoresist. The electron blocking layer was applied by spin coating 50 nm of poly(3,4-ethylene dioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) (Baytron P AL 4083, HC Stark) at 3,000 rpm for 45s. The coated samples were baked at 120 °C for 15 min and then moved to a nitrogen-filled glove box. Regioregular P3HT (15mg/ml, Rieke Metals, Inc.) and PCBM (Nano-C, Inc.)

were dissolved in 1,2-dichlorobenzene (DCB) with mixture of a 1:0.8 weight ratio. The blend was stirred overnight at 40 °C in the glove box. The active layer was deposited by spin-coating at 600 rpm for 1 min and annealed at 80 °C for 30 min while keeping the structure inside a nitrogen-filled glove box. The structure was transferred into a thermal evaporator; total exposure to air was typically less than 20 minutes. The thermal evaporator was used to apply a 1nm thick lithium fluoride (LiF) tunneling layer and a 100 nm thick aluminum cathode. A laser cut stencil mask was used in the final deposition process. The stencil mask had a 4 mm wide and 1.5 cm long opening and was oriented to be perpendicular to the previously-patterned ITO strips to contact the five domains. Each matrix element had an active area of 0.02 cm^2. Current-voltage characteristics were measured using a Keithley 6517A electrometer. All electrical measurements were performed in a nitrogen atmosphere. A broadband high intensity discharge lamp (Philips MASTERColour CDM-R/830) was used to simulate the sunlight at an irradiance of 100 mW/cm^2, which was calibrated by using a photometer (International Light Technologies, ILT1400A); this lamp has been reported before[1] to be a good match for simulated solar illumination. The reflectance absorption spectrum was analyzed using an optical fiber VIS-NIR spectrophotometer (Ocean Optics, USB4000 VIS-NIR, QR400-7-UV-VIS). The reflectance absorption spectrum of bare ITO glass was collected and used for the background correction.

Supplementary Figures

Figure S1 shows scanning electron microscope images of electrically controlled localized Pt deposits after (a) 40s, (b) 60s, and (c) 120s deposition time. The deposits are formed using an array of 1 μm wide and 500 nm deep holes in a Microposit S1805 photoresist which acts as a guide before the material reaches the biased ITO domain that is used to control the material flux. The material is funneled into a location which is roughly 10x smaller than the 1 μm wide opening itself leading to a diameter of 110 nm. The diameter of the nanowires begins to increase as they grow much taller than the photoresist guides themselves. For example after deposition for 120s the structures have grown 1.5 μm tall which is 3 times the thickness of the 500 nm thin photoresist and the onset of broadening (mushrooming) becomes visible. As a design rule, structures will lack broadened tops if the deposition process is stopped before the towers significantly exceed the height of the photoresist film thickness itself.

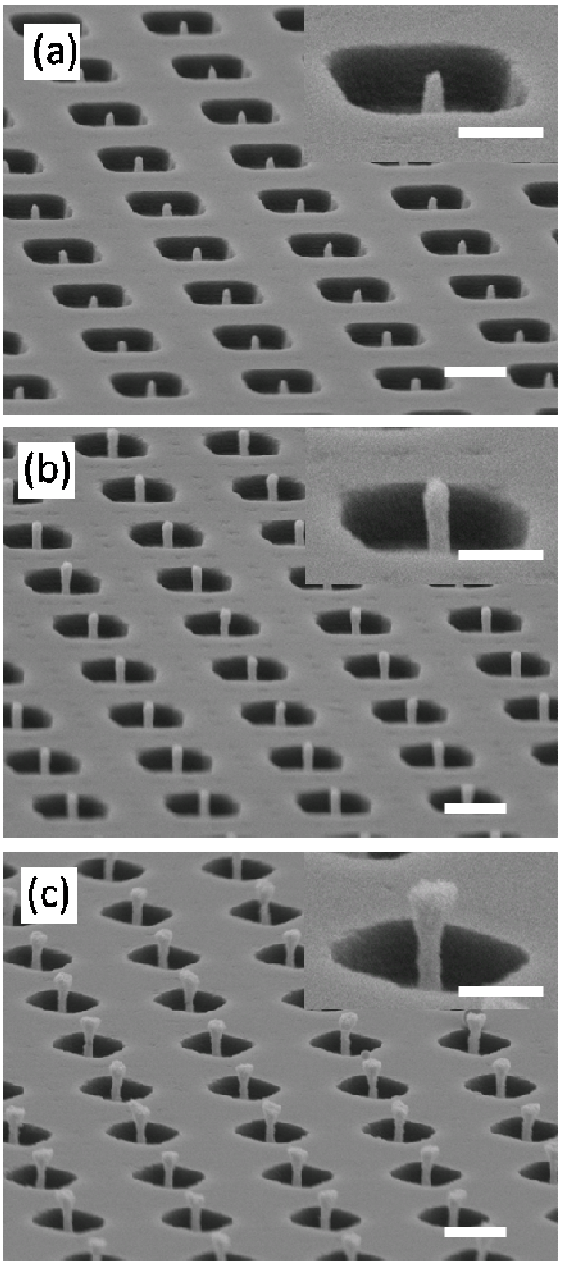

Figure S1. *SEM of localized Pt deposits after (a) 40s, (b) 60s, and (c) 120s deposition time. 1 μm scale bars in (a-c) and 500 nm scale bars in the insets.*

The deposits shown in the manuscript are made out of very small, typically < 5 nm Pt, Ag and W single crystal particles, which were confirmed by analyzing the deposits using high resolution transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). For completeness the data for tungsten is shown in Figure S2**.** Platinum and silver were discussed in the main body.

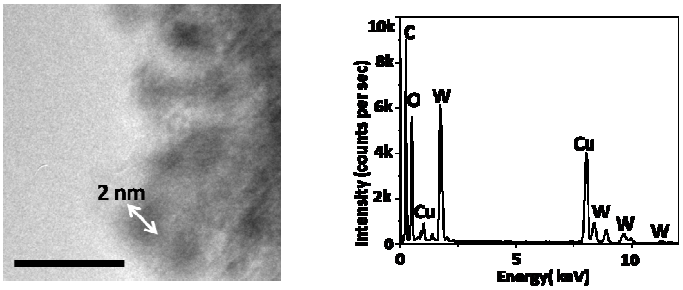

Figure S2. *TEM and EDS data of tungsten particles. 5 nm scale bar.*

Figure S3 shows the histogram with the measured variation in height in domain 5. The standard deviation (STD) was less than 13.1 nm for the 800 nm tall structures.

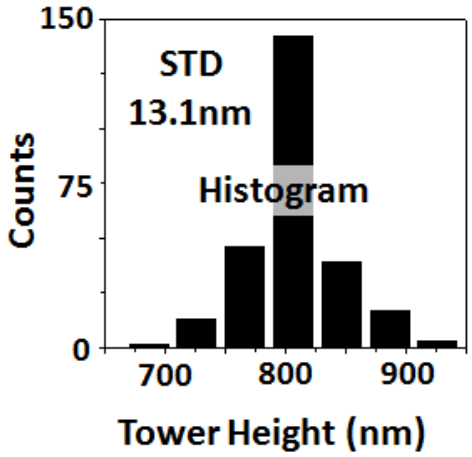

Figure S3. *histogram of height that centers around 806 nm.*

Figure S4 provides a larger area view of deposits after (a) deposition of Pt nanowires, (b) removal of photoresist guides, and (c) deposition of the thin film stack that is required to complete the solar cells. The completed device in (c) depicts about 1,000 deposition sites. Out of the 1,000 deposition sites, 5-6 sites are slightly elevated, and 1 site shows a defect where one of the 100 nm in diameter and 800nm tall nanowires is missing likely because it failed to withstand the spin coating step.

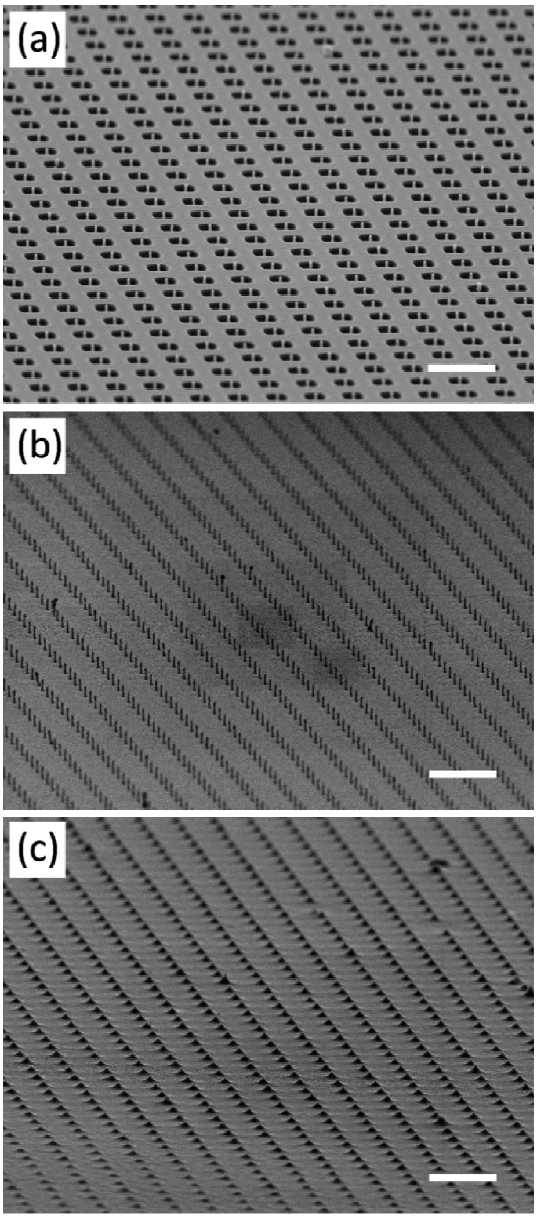

Figure S4. *Large area views used to analyze defect rates after (a) deposition of Pt nanowires, (b) removal of photoresist guides, and (c) deposition of the thin film stack. 5 μm scale bars.*

Figure S5 provides the photovoltaic cell processing steps, the final photovoltaic cells on 5 different domains and the energy level diagram. Figure S5(a) shows the processing steps, the respective SEMs that are required to complete the devices. The steps are: 1. nanowire deposition using photoresist guides and bias control, 2. removal of the photoresist guides using an oxygen plasma, 3. spin coating of the electron blocking layer (PEDOT: PSS), active blend layer (P3HT: PCBM), and 4. vapor deposition of lithium fluoride (LiF) tunneling layer and aluminum top contact. Figure S5(a1-a5) showed the SEM images of the completed photovoltaic cells on five different domains and also depicted the respective short circuit current density for each domains. The energy level diagram and film thickness are illustrated in figure S5(b).

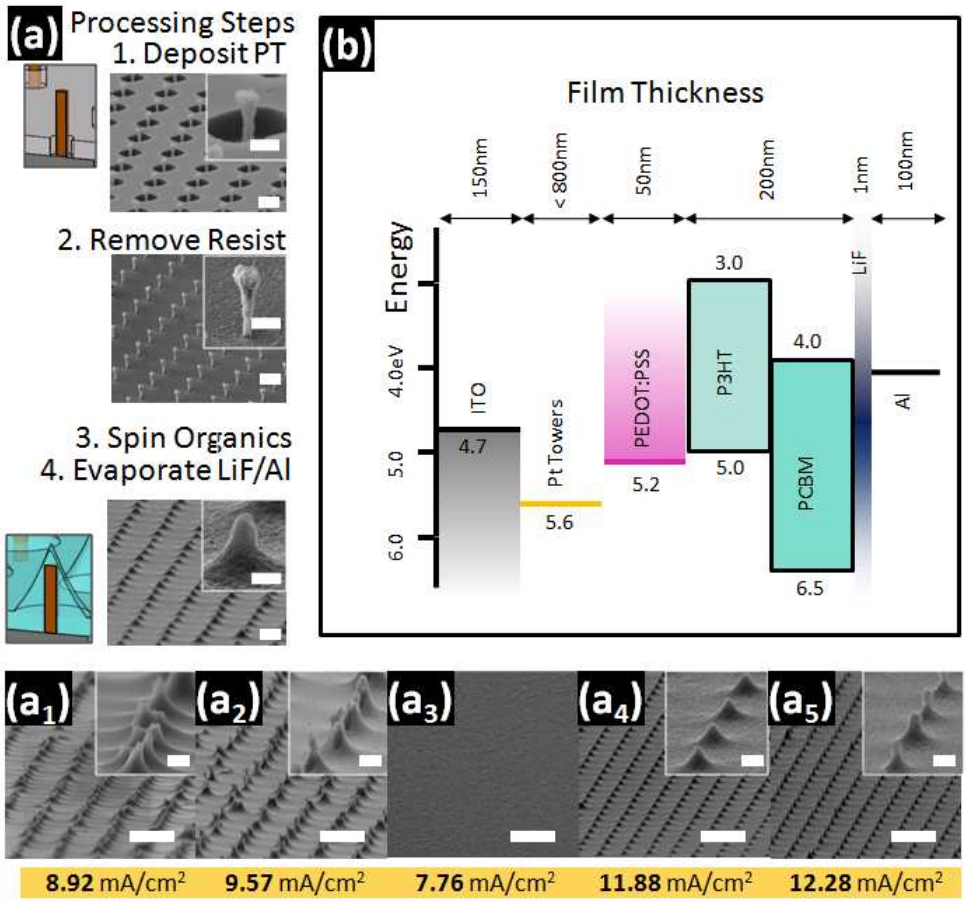

Figure S5. *(a) Processing steps to complete the photovoltaic cells leading to the recorded short circuit current densities that improve for long and dense nanowire arrays. (a1-a5) The SEM images of complete photovoltaic cells in domain 1 to 5. (b) the energy level diagram and film thickness. 1 µm scale bars in (a). 300 nm scale bars in insets of (a). 5 µm scale bars in (a1-a5). 300 nm scale bars in insets of (a1)-(a5)*

Supplemental Reference

1. Colsmann, A.; Junge, J.; Kayser, C.; Lemmer, U. *Applied Physics Letters* **2006,** 89, 203506.