

## II.G.18 Joint Center for Artificial Photosynthesis: Si Microwire-Based Solar Water Splitting Devices

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conversion efficiencies were very low, 0.0068% and 0.0019% when the cathode compartment was saturated with Ar or H<sub>2</sub>, respectively, due to the non-optimal photovoltage and band-gap of the WO<sub>3</sub> that was used in the demonstration system to obtain stability of all of the system components under common operating conditions while also insuring product separation for safety purposes.

### Introduction

Si microwire array photocathodes have been shown to generate photovoltages in excess of 500 mV in acidic aqueous environments, and provide a preferred geometry, relative to planar structures, for devices that effect the unassisted generation of fuels from sunlight. Microwire arrays benefit from orthogonalization of the directions of light absorption and minority-carrier collection, as well as from light-trapping effects, an increased surface area for catalyst loading per unit of geometric area, a small solution resistance as compared to planar designs, a reduced material usage through reusable substrates, and the ability to embed the microwires into ion-exchange membranes that exhibit little permeability to H<sub>2</sub> and O<sub>2</sub>, thereby producing flexible devices that persistently separate the products of the water-splitting reaction. However, the voltage generated from single-junction Si microwire arrays is much lower than the 1.23 V required for solar-driven water splitting, so a wider band-gap partner light absorber must be introduced electrically in tandem (Si/partner tandem device), to generate useful current at voltages that exceed the thermodynamically required values for fuel production. Accordingly, tandem-junction devices offer the highest theoretical and experimentally realized efficiencies for solar-driven water splitting through additive voltages across two photoabsorbers that use the solar spectrum more effectively.

In addition to band gap considerations for a Si/partner tandem system, achieving the desired electronic behaviour at the interface between Si and its tandem partner presents a significant challenge for production of an integrated solar fuels generation device. The materials must be mutually compatible and generally must operate in a single, concentrated (1.0 M) aqueous electrolyte. TiO<sub>2</sub>, WO<sub>3</sub>, BiVO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> are stable in concentrated aqueous electrolytes and form suitable tandem partners for Si. However, Si is stable only in acidic aqueous environments, limiting the presently available partner materials that are stable under such conditions to only TiO<sub>2</sub> and WO<sub>3</sub>. WO<sub>3</sub> is the preferred material because of its smaller band gap (E<sub>g</sub> = 2.6 eV) and significant photocurrent response to visible-light illumination. The electronic behaviour of the

### Objectives

The mission of the Joint Center for Artificial Photosynthesis (JCAP) is to produce fundamental scientific discoveries and major technological breakthroughs to enable the development of energy-efficient, cost-effective, and commercially viable processes for the large-scale conversion of sunlight directly to fuels. JCAP's 5-year goal is discovery of robust, Earth-abundant light absorbers, catalysts, linkers, membranes, and scale-up science required to assemble the components into a complete artificial photosynthetic system. The Membranes and Mesoscale group within JCAP is focused on membrane development for solar fuels devices and design, modeling, fabrication and characterization of integrated device components on the micro- and nano-scopic scale. One design currently being pursued and presented here is a tandem junction device based on Si microwire arrays and a second absorber conformally coating each individual microwire, which is all embedded and supported in an ionic transport membrane.

### Abstract

Tandem junction (n-p<sup>+</sup>-Si/ITO/WO<sub>3</sub>/liquid) core-shell microwire devices for solar-driven water splitting have been designed, fabricated and investigated photoelectrochemically. The tandem devices exhibited open-circuit potentials of E<sub>OC</sub> = -1.21 V versus E<sup>0</sup>(O<sub>2</sub>/H<sub>2</sub>O), demonstrating additive voltages across the individual junctions (n-p<sup>+</sup>-Si E<sub>OC</sub> = 0.5 V versus solution; WO<sub>3</sub>/liquid E<sub>OC</sub> = -0.73 V versus E<sup>0</sup>(O<sub>2</sub>/H<sub>2</sub>O)). Optical concentration (12x, AM1.5D) shifted the open-circuit potential to E<sub>OC</sub> = 1.27 V versus E<sup>0</sup>(O<sub>2</sub>/H<sub>2</sub>O) and resulted in unassisted H<sub>2</sub> production during two-electrode measurements (anode: tandem device, cathode: Pt disc). The solar energy-

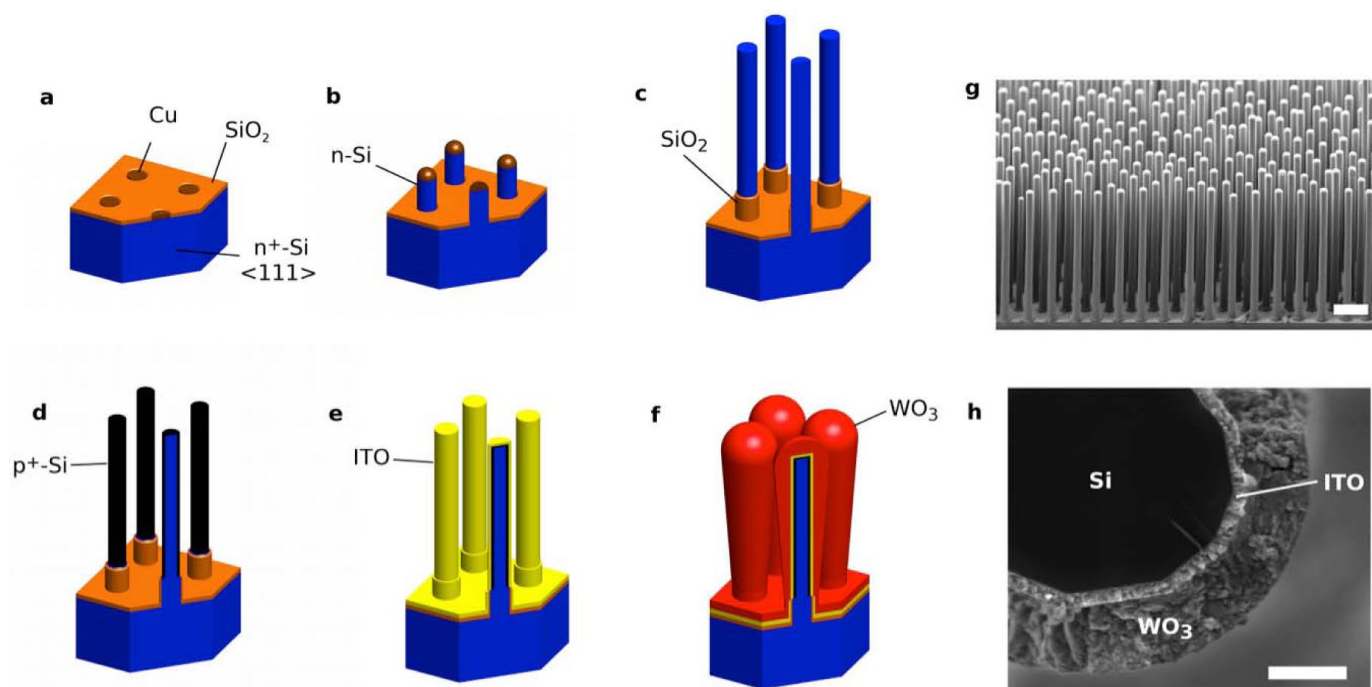
Si/  $\text{WO}_3$  interface has recently been shown to be non-ohmic, but addition of an intermediate tin-doped indium oxide (ITO) layer has been shown to provide low resistance, ohmic behaviour between p-type, or  $\text{p}^+$ -type, Si and  $\text{WO}_3$ .

We present a tandem core-shell photoelectrochemical device that consists of a periodic array of buried homojunction  $\text{n-p}^+$ -Si microwires that have been sequentially coated with a radial sheath of ITO and  $\text{WO}_3$ . When immersed in air-saturated 1.0 M  $\text{H}_2\text{SO}_4$ , the dual radial-junction microwire structure enables efficient carrier collection from both the Si and  $\text{WO}_3$  light absorbers, despite short minority-carrier diffusion lengths, i.e.,  $\sim 10$  micrometers in Si and  $\sim 1$  micrometers in  $\text{WO}_3$ . A necessary feature of this tandem architecture is the incorporation of the ITO layer between the Si and  $\text{WO}_3$  light-absorbing materials. This ohmic contact layer ensures facile, low-resistance carrier transport between the Si and  $\text{WO}_3$  and relaxes the requirements for proper band alignment between the  $\text{p}^+$ -Si emitter and the  $\text{WO}_3$ . Transparent conductive oxides, such as FTO or ITO, are commonly used as back contacts to semiconductor metal oxides; thus this design is expected to be robust towards implementation of newly discovered materials, because the ITO layer will be amenable to many different Si tandem partner absorbers.

## Results

Fig. 1a–f depicts the process used to fabricate the on-wafer devices used herein. Fig. 1g displays an image of a completed wire-array device, while Fig. 1h shows a cross-section of a single wire demonstrating the layered device structure. The Si microwires were 40–70 micrometers in length, had a diameter of  $\sim 2$  micrometers and had doping densities on the order of  $10^{17} \text{ cm}^{-3}$ . Secondary-ion mass spectrometry data from planar samples indicated that the  $\text{p}^+$ -Si emitter thickness was  $\sim 200$  nm. The sequential, conformal layers of ITO and  $\text{WO}_3$  were  $\sim 100$  nm and  $\sim 400$  nm, respectively.

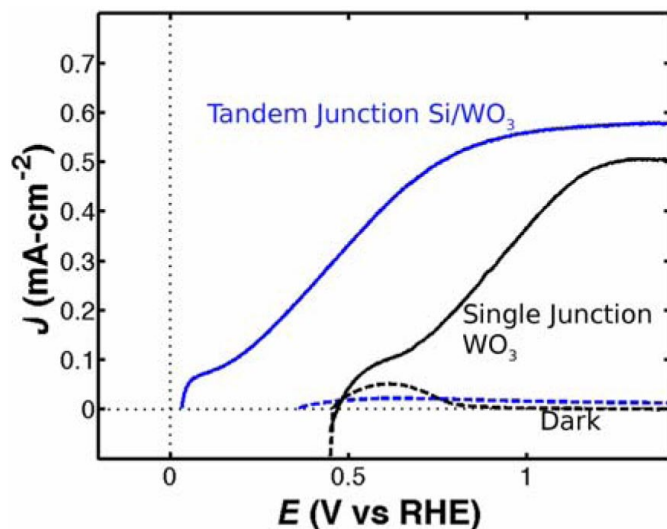
Device operation proceeds through photoexcitation of electrons and holes where photoexcited majority-carrier electrons in the n-Si core are transported axially to the back contact through the degenerately doped substrate ( $\text{n}^+$ -Si) to perform the hydrogen-evolution reaction (HER) at a Pt counter electrode, while photoexcited minority-carrier holes are collected radially in the  $\text{p}^+$ -Si sheath. The holes in Si recombine with photoexcited majority-carrier electrons from the n- $\text{WO}_3$  at the ITO contact, while minority-carrier holes that are photoexcited in the n- $\text{WO}_3$  are collected at the liquid interface and drive the oxidation of water or anolyte.



**FIGURE 1.** (a) Photolithographically patterned  $\text{n}^+$ -Si  $\langle 111 \rangle$  wafer with a  $\text{SiO}_2$  mask layer and Cu catalyst in the desired growth pattern. (b) VLS Cu-catalyzed growth of n-type Si microwires on an  $\text{n}^+$ -Si substrate followed by a metal etch (RCA 2). (c)  $\text{SiO}_2$  diffusion barrier (boot) formation via  $\text{SiO}_2$  growth, PDMS infill, HF etch and PDMS removal. (d)  $\text{p}^+$ -Si emitter drive-in from  $\text{BCl}_3$  precursor at  $950^\circ\text{C}$  for 30 min in a CVD furnace. (e) Conformal DC sputter coating of ITO. (f) Conformal n- $\text{WO}_3$  electrodeposition and annealing at  $400^\circ\text{C}$  for 2 h. (g) Fully assembled tandem junction device array SEM (scale bar = 10 micrometers). (h) Cross-sectional SEM of a fully assembled tandem junction single wire demonstrating the layered structure of the device (scale bar = 500 nm).

Fig. 2 shows the photoelectrochemical behaviour of single junction (p-Si/ITO/n-WO<sub>3</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub>) and tandem junction (n-Si/p<sup>+</sup>-Si/ITO/n-WO<sub>3</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub>) microwire array devices under simulated one Sun illumination conditions. The p-Si/ITO and p<sup>+</sup>-Si/ITO contacts have been shown to produce ohmic behaviour allowing isolation of the n-WO<sub>3</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub> liquid junction performance in the single junction case and efficient use of the buried n-p<sup>+</sup>-Si junction in the tandem junction case. The single- and tandem-junction microwire devices exhibited  $J = 0.50 \text{ mA cm}^{-2}$  and  $J = 0.58 \text{ mA cm}^{-2}$ , respectively, at the formal potential for oxidation of water to O<sub>2</sub>,  $E^{0'}(\text{O}_2/\text{H}_2\text{O})$ . The first peak in photocurrent density is a dark redox process that results in the photochromism of WO<sub>3</sub>, whereupon reverse scans the WO<sub>3</sub> film is reduced through proton intercalation, and is subsequently oxidized on the forward scan. The second peak is associated with photocurrent that results in actual solution redox reactions.

The open-circuit potentials were  $E_{\text{OC}} = -0.73 \text{ V vs. } E^{0'}(\text{O}_2/\text{H}_2\text{O})$  and  $E_{\text{OC}} = -1.21 \text{ V vs. } E^{0'}(\text{O}_2/\text{H}_2\text{O})$  for the single- and tandem-junction devices, respectively. The  $E_{\text{OC}}$  for the WO<sub>3</sub>/liquid contact is in accord with expectations for WO<sub>3</sub> photoanodes operating under these conditions. The 0.48 V shift in  $E_{\text{OC}}$  of the tandem junction device relative to the single junction device is therefore attributable to the presence of the n-p<sup>+</sup>-Si buried junction in the tandem device and is consistent with non-aqueous photoelectrochemical performance of n-p<sup>+</sup>-Si buried junction microwire arrays.



**FIGURE 2.** Three electrode photoelectrochemical (forward scan, scan rate =  $20 \text{ mV s}^{-1}$ ) performance for single (black) and tandem (blue) junction microwire devices in contact with  $1.0 \text{ M H}_2\text{SO}_4(\text{aq.})$ . The single junction microwire device consisted of WO<sub>3</sub> supported on p-Si microwires that had been coated with ITO. Here the p-Si/ITO contact is ohmic so the only rectifying junction is at the WO<sub>3</sub>/liquid junction. These data demonstrate the presence of an additive voltage from each junction, with 0.73 V and 0.5 V produced by the WO<sub>3</sub>/liquid and n-p<sup>+</sup>-Si buried junctions, respectively.

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Under modest optical concentration (12 Suns, AM1.5D), tandem junction microwire-array devices exhibited  $E_{\text{OC}} = -1.27 \text{ V vs. } E^{0'}(\text{O}_2/\text{H}_2\text{O})$ , which exceeds the 1.23 V potential difference necessary for unassisted water splitting under standard-state conditions. Chronoamperometric measurements were performed with a two-electrode setup at 0 V applied bias between an illuminated tandem junction WO<sub>3</sub>/Si microwire array device and a Pt disc electrode. The devices produced solar-to-hydrogen energy-conversion efficiencies of 0.0068% ( $6.5 \times 10^{-3} \text{ mA}$ ,  $0.060 \text{ mA-cm}^{-2}$ ) and 0.0019% ( $1.9 \times 10^{-3} \text{ mA}$ ,  $0.017 \text{ mA-cm}^{-2}$ ) when the Pt disc was in contact with Ar(g)- and H<sub>2</sub>(g)-saturated solutions, respectively. Product analysis was performed separately on the oxidation and reduction products in  $1.0 \text{ M H}_2\text{SO}_4$ . In contact with H<sub>2</sub>SO<sub>4</sub> (aq.), sulfate (SO<sub>4</sub><sup>2-</sup>) is preferentially oxidized to peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) at the WO<sub>3</sub>/liquid interface, which was confirmed as an oxidative product by ultraviolet-visible absorption spectroscopy as published previously. Although direct oxygen evolution was not realized due to the slow O<sub>2</sub> evolution kinetics of WO<sub>3</sub>, peroxydisulfate has been shown to stoichiometrically evolve O<sub>2</sub> using Ag<sup>+</sup> as a catalyst. At the Pt disc cathode, H<sub>2</sub>(g) production was detected by mass spectrometry of the reaction products when the operational current density was passed at the Pt disc electrode. Due to the small amount of H<sub>2</sub>(g) produced, direct quantification of the faradaic efficiency was not performed, however no other products are expected due to the use of trace metal grade H<sub>2</sub>SO<sub>4</sub>.

## Future

Integration of new photoanode materials in place of WO<sub>3</sub> has the potential to increase the performance of the tandem device by producing more negative  $E_{\text{OC}}$  values as well as much larger values of the current density at  $E = E^{0'}(\text{O}_2/\text{H}_2\text{O})$ . To produce a more negative value of  $E_{\text{OC}}$ , the potential of the conduction band of the anode material must be more negative than the potential of the conduction band of WO<sub>3</sub>, i.e. closer to the vacuum level, thereby increasing the barrier height at the semiconductor/ liquid junction. Recent studies of mixed-metal oxides have demonstrated photoanode materials with smaller electron affinities than WO<sub>3</sub>. The production of increased current density at  $E = E^{0'}(\text{O}_2/\text{H}_2\text{O})$  will require lowering the recombination rates, by improving the material quality and passivating surface states, as well as the discovery of narrower band-gap materials that are stable under oxidizing conditions. Additionally the anodes must be stable under conditions where the cathode and membrane materials are stable, and under conditions where the membrane exhibits high transference numbers for protons, to allow for effective, passive neutralization of the pH gradient between the sites of water oxidation and water reduction while maintaining product separation for intrinsically safe operation of the system under varying levels of illumination.

**Publication list (including patents)  
acknowledging the DOE grant or contract**

1. Shaner, M.R. *et al.* Photoelectrochemistry of core–shell tandem junction n–p+–Si/n–WO<sub>3</sub> microwire array photoelectrodes. *Energy Environ. Sci.* **2014**, *7* (779)

1. Patent Application: Semiconductor Structures for Fuel Generation, April 3, 2013, Shane Ardo, et. al.