Photoelectrochemical Characterization of Si Microwire Array Solar Cells

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Abstract — **Many proposed next-generation photovoltaic devices have complicated nano- and micro-structured architectures that are designed to simultaneously optimize carrier collection and light absorption. Characterization of the electrical properties of these highly structured materials can be challenging due to the difficulty of creating electrical contacts, as well as the need to decouple the properties of the contact from that of the semiconductor. Regenerative photoelectrochemistry is a powerful technique to characterize the electrical properties of such systems, providing a conformal liquid contact that can be ohmic or rectifying, depending on the system used.**

We demonstrate the use of the methyl viologen regenerative electrochemical system to characterize different stages of the fabrication of radial junction Si microwire (SiMW) solar cells. Photoelectrochemical characterization, combined with other more traditional measurements allows evaluation of how the different processing steps affect the device performance, without having to construct a fully integrated device. We describe the operating principle of this technique, and demonstrate that it can be applied to semiconductor materials with complex architectures.

Index Terms — **material characterization, Silicon microwire, photoelectrochemistry, photovoltaic.**

I. INTRODUCTION

Micro and nano-structured semiconductors are promising materials for the next generation of low-cost, high-efficiency photovoltaic devices. Structured materials can decouple the processes of light absorption and carrier collection, allowing inexpensive materials with short minority carrier diffusion lengths to effectively capture photoexcited carriers [1]. Control over the geometry of these devices can also enhance their absorption relative to thin-film structures [2, 3]. Characterization of the electrical properties of highly structured materials can be challenging due to the difficulty of creating electrical contacts, as well as the need to decouple the properties of the contact from that of the semiconductor. Many of these materials are grown using different techniques than those used for planar material, so non-destructive electrical measurements are needed to understand the doping densities, diffusion lengths, etc. at various stages of device fabrication. The use of a liquid-junction allows for the creation of a conformal electrical contact without needing to deposit transparent conductors or contact grids. We describe herein the photoelectrochemical characterization of silicon microwire (SiMW) photovoltaics, which are a promising material for use in high-efficiency, wafer-less photovoltaics [4, 5].

Regenerative photoelectrochemistry provides a useful platform for comparing the device performance at different stages of fabrication. This technique is applicable to other semiconductor systems as well, and thus provides a tool for understanding the material quality without the need to create a full solar cell device.

II. SEMICONDUCTOR-LIQUID CONTACTS

In a regenerative photoelectrochemical system, a redox couple (consisting of a donor/electron pair with rapid charge-transfer kinetics) is dissolved in a liquid electrolyte. The electrochemical potential, E(A/A⁻) i.e. the Fermi level, of the liquid phase is given by the Nernst equation (1):

$$E(A/A^-) = E^{o'}(A/A^-) + (kT)\ln\left(\frac{[A]}{[A^-]}\right) \quad (1)$$

where $E^{o'}$(A/A⁻) is the formal potential of the redox couple under standard conditions, and the second term in the equation accounts for differences in concentration of the donor/acceptor forms of the redox couple. As in a solid-state Schottky diode, the Fermi level of the semiconductor will equilibrate with that of the contacting liquid phase, with most of the charge dropping across the semiconductor, inducing band bending within the semiconductor [6].
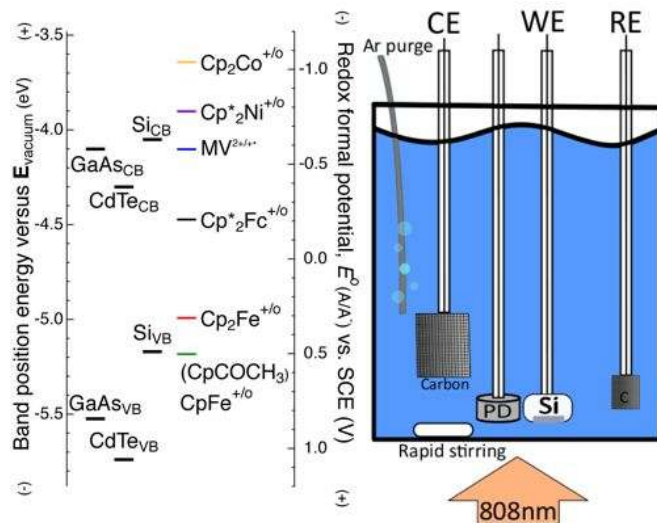

Fig. 1. (left) Energetics of different semiconductor band edges and redox couples. (right) Schematic of a MV²⁺/⁺ photoelectrochemical cell: the semiconductor material is the working electrode (WE) and the PD represents the photodiode used to monitor the light intensity.

The barrier height of the resulting junction is given by the difference between the Fermi level of the semiconductor and the liquid phase. The choice of the redox couple and electrolyte system is based on the stability of the semiconductor and the desired barrier height of the system. Not all semiconductor-liquid systems exhibit stable, ideal diode behavior, but a variety of materials have been well characterized by electrochemical methods in the literature: Si [7, 8], InP [9], GaAs [10], CdX (X = Te, Se, S) [11]. Fig. 1a shows the formal potentials of a variety of different redox couples that have been used to photoelectrochemically characterize semiconducting materials [12].

Methyl viologen ($MV^{2+/+}$) is a one-electron, outer-sphere, redox couple that can be used in both aqueous and non-aqueous electrolytes. This system has previously been used to investigate the performance of p-SiMW arrays as grown [13] and after the introduction of an n^+ emitter [14]. Due to its work function (which corresponds to -0.67 V vs. a saturated calomel electrode (SCE)), $MV^{2+/+}$ generally forms a high barrier height with p-type semiconductors, and forms an ohmic contact to n-type systems. Because the solution potential determined from (1) depends on the relative concentrations of the reduced and oxidized forms of the redox couple, both species must be present in the solution to extract stable photovoltage measurements. The MV^+ species is highly absorbing at most visible wavelengths, so measurement of the photovoltage relative to a well-defined solution potential, one that will not vary with small changes in the relative concentrations of MV^{2+} and MV^+, requires an illumination source that is not absorbed by solution. Monochromatic 808 nm illumination from a diode laser has been successfully used with Si devices [13]. To monitor the illumination intensity incident onto the sample, a photodiode is placed in the solution at a height parallel to that of the sample (Fig. 1b). The system can also be operated with very small amounts of the reduced MV^+, to confirm short-circuit behavior using simulated sunlight. 60mW cm^{-2} of 808nm illumination produces short-circuit current densities for planar Si devices comparable to those under AM1.5G illumination, so such conditions provide a good indication of device performance under 1 sun illumination.

III. FABRICATION OF SiMW SOLAR CELLS

Regenerative photoelectrochemistry has been important in the development of Si microwire-based radial pn junction solar cells [2, 13, 15]. These devices, grown from $SiCl_4$ and BCl_3 using the vapor-liquid-solid (VLS) process with a Cu catalyst, have demonstrated promising efficiencies as flexible, wafer-free photovoltaics [5, 16]. The process for fabrication of a radial junction device is outlined in Fig. 2A.

Wires were first grown using the VLS process with a Cu catalyst (i). The Cu was then removed using an RCA2 etch (ii), and a thermal oxide was grown over the entire sample. The bases of the wires were protected with a polymer infill

(iii), and then the oxide was etched from the top of the wires using HF (iv). An n^+ emitter layer was formed using a solid-state P source to dope the outer 100-200 nm of the wires (v). The array was then infilled with a polymer (vi), and a top-contact was made using seeded metal nanoparticles and Ag-nanowires (AgNW not shown in schematic) [17]. As the SiMW arrays were processed, small pieces were cut off of the larger sample. Electrodes with areas 0.05-0.1cm^2 were fabricated from these pieces by contacting the back of each sample with Ga/In eutectic and sealing the edge of the samples with epoxy.
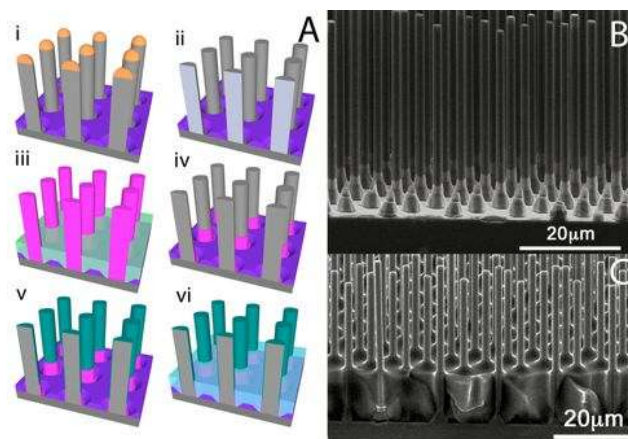

Fig. 2. A - Schematic of radial junction SiMW solar cell fabrication. B - SEM image of p-SiMW with oxide boots (stage *iv*). C - SEM image of polymer-embedded pn junction SiMWs (stage *vi*).

IV. PHOTOELECTROCHEMICAL CHARACTERIZATION OF RADIAL JUNCTION SiMW SOLAR CELLS

The regenerative methyl viologen ($MV^{2+/+}$) photoelectrochemical system was used to evaluate the figures of merit: open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (*FF*), and efficiency, at each stage of processing. A three-electrode system (Fig. 1) was used in which the potential of the sample was measured relative to a carbon reference electrode, and current was passed through a carbon counter electrode. Electrochemistry was performed using 50 mM of MV^{2+} in a pH 3 potassium hydrogen phthalate buffer with 0.5 M of K_2SO_4 as the supporting electrolyte [13]. The MV^+ species was generated *in-situ* to maintain a solution potential of -0.58 to -0.60 V vs. SCE (~3 mM MV^+). The electrochemical cell was stirred rapidly to maintain high concentration of the redox couple at the electrode surface. The cell was purged with Ar during experiments due to the O_2 sensitivity of the MV^+ species.

A. Data Correction

Although the experimental set-up allowed for the rapid screening of multiple semiconductor samples, the geometry of the cell (Fig. 1) introduced a dependence of the measured

electrical performance on the mass transport of the redox species through the liquid electrolyte. These mass transport effects create concentration overpotential losses in the cell. These losses, along with series resistance losses in the electrolyte, decrease the apparent performance of the photoelectrode relative to its true performance. Standard electrochemical methods allow for the correction of these artifacts to isolate the performance of the semiconductor, and thus provide a more accurate measurement of how the material would behave in a photovoltaic system [18]. To perform the corrections, the limiting anodic and cathodic currents, measured using a metallic electrode in the same position as the semiconductor sample, are used to calculate the series resistance loss of the liquid. The voltage is then corrected at each (*J*, *V*) data point using the equations below (2-3), where $J_{l,a}$ and $J_{l,c}$ are the limiting anodic and cathodic currents (respectively), *n* is the number of electrons transferred during the redox process ($n=1$ for $MV^{2+/+}$), R_{cell} is the measured cell resistance, *i* is the measured current density.

$$\eta_{corr} = \frac{k_B T}{nq}\left[\ln\left(\frac{J_{l,a}}{J_{l,c}}\right) - \ln\left(\frac{J_{l,a}-J}{J-J_{l,c}}\right) \right] \quad (2)$$

$$E_{corr} = E - iR_{cell} - \eta_{conc} \quad (3)$$

Fig. 3 shows the relative performance of a wire array with diameters of 2 μm, heights of 60 μm, in a square geometry with a 7 μm pitch, in stages *iv* and *v* of device processing. The raw data are represented as dotted lines, and the corrected data as solid lines. The introduction of a radial pn junction increased the photovoltage of the device from 450 mV to 490 mV, but slightly lowered the J_{sc}. This drop in current density can be explained by the decrease in photoactive area, because
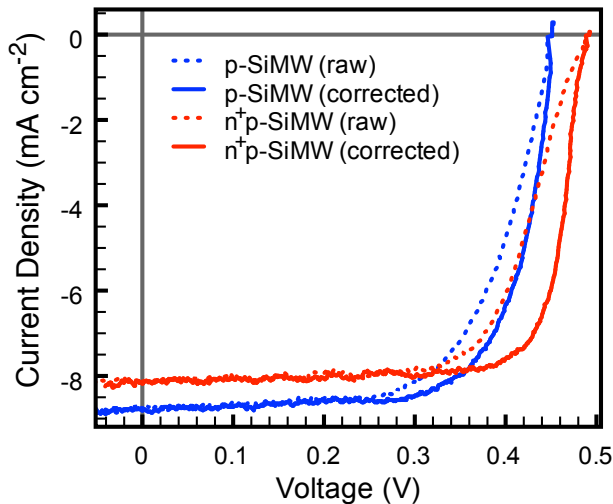
even 100 nm of a conformal n+ emitter over a 2 μm diameter wire decreases the volume of the lightly doped p-type absorber by 10%. Spreading resistance measurements and 4-point probe measurements on planar samples that were processed in parallel with the wire arrays and indicated an emitter thickness of 100-150 nm and a P doping level of ~10^{19} cm^{-3}.

The data correction (Fig. 3. solid lines) did not affect the values of J_{sc} or V_{oc}, but improved the fill factor by squaring up the curve near open-circuit. In our $MV^{2+/+}$ system, $J_{l,a}$ is much lower than $J_{l,c}$ because less of MV^+ is present in solution than MV^{2+}. This creates a concentration overpotential effect that appears as a series resistance in the *J-V* data, but in actuality is not related to the fundamental semiconductor performance.

B. Evaluation of Performance During Device Processing

Semiconductor photoelectrochemistry also allows for high-throughput characterization of the effects of variation of a single parameter of interest such as the length of the wires or the doping density. Such experiments allow for optimization of a material parameter without the need for subsequent processing. Fig. 4 shows a comparison of three different p-SiMW arrays that were grown from the same substrate, under the same conditions, but for different periods of time, resulting in different wire heights. The current density increased with the length of the SiMWs: J_{sc} = 4.8 mA cm^{-2} (H= 60 μm), 8.1 mA cm^{-2} (H= 120 μm), 10.0 mA cm^{-2} (H= 150 μm). The measured V_{oc} values are not identical for these samples, but only vary from 405 mV to 440 mV relative to the solution potential, similar to previous reports [13].
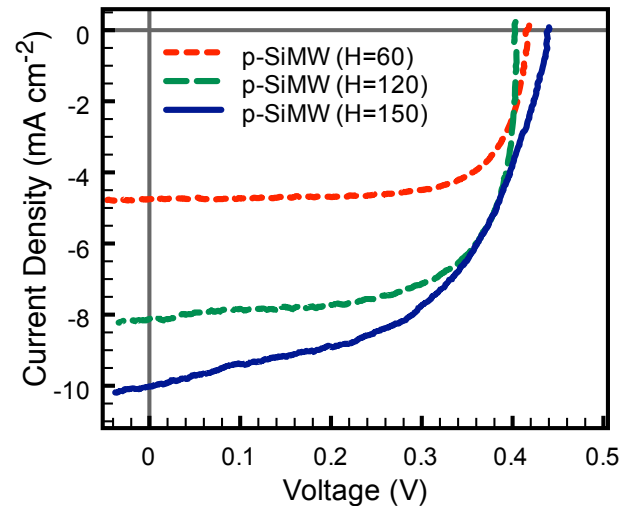

Fig. 3. Electrochemical *J-V* data for a SiMW array before (blue) and after (red) n+ emitter formation. All of the data were collected under 60 mW cm^{-2} of 808 nm illumination. The raw data is represented by the dashed lines, and the solid lines show the data corrected using (2-3).

Fig. 4. Electrochemical *J-V* data for SiMW arrays of varying heights: 60, 120, and 150 μm. All wires were grown from the same substrate and had diameters of 1.8-2 μm. All of the data were collected under 60 mW cm^{-2} of 808nm illumination.

A liquid contact can also be used to decouple inherent properties of the semiconductor from effects due to formation

of the top contact material or other processing steps. Fig. 5 compares the performance of a SiMW array solar cell characterized using methyl viologen electrochemistry relative to the measured performance of the final solid-state device. The blue curve shows the data of the p-SiMW (stage *iv*), and the red curve depicts the performance of the polymer-embedded pn junction in contact with $MV^{2+/+}$. The light and dark data for the polymer-embedded solid-state device with a AgNW based top contact (Fig. 6) are shown by the black solid line and the navy dotted line, respectively [17]. The figures of merit for each of the devices are depicted in Table 1.
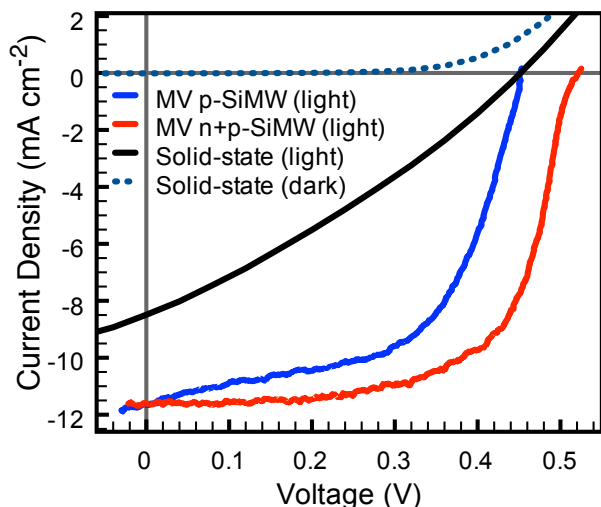
Fig. 5.   *J-V* data for the same SiMW array at different stages of device processing. The blue and red curves show $MV^{2+/+}$ data collected under 60 mW cm^{-2} of 808nm illumination; the solid-state measurements were performed under 100 mW cm^{-2} of AM1.5G illumination.

Device Type	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	η 808/AM1.5
MV: p-SiMW	453	11.6	0.57	5.0%
MV: n$^+$p-SiMW (infilled)	521	11.6	0.65	6.3%
Solid State n$^+$p SiMW	440	8.49	0.33	1.22%

Table 1.   Performance characteristics of devices at different processing stages. The efficiencies for $MV^{2+/+}$ devices are based on 808 nm illumination while the solid-state devices are based on 100 mW cm^{-2} of AM 1.5G illumination.

The introduction of a pn junction increased the V_{oc} measured photoelectrochemically by ~70 mV, and also improved the fill factor. The electrical properties of this sample were measured with the wires infilled with polymer, which tended to increase the absorption due to increased scattering, so the decrease in photocurrent noted in Fig. 3 was not as significant here. The light-beam-induced current (LBIC) map in Fig. 6 showed that the current density was not uniform across the sample, but LBIC cannot quantify the fundamental cause of the performance loss. The solid-state data shown in Fig. 5, while not indicative of the best cells measured in our labs, exhibited

much lower V_{oc} and fill factors then the same device measured photoelectrochemically before addition of the top contact. This behavior demonstrates that the top-contact, and not the material quality of the SiMW array or doping profile, is limiting device performance. The fabrication of good contacts to highly structured photovoltaic materials can be challenging, so it is useful to be able to monitor the semiconductor device quality independent of the choice of contacting material.
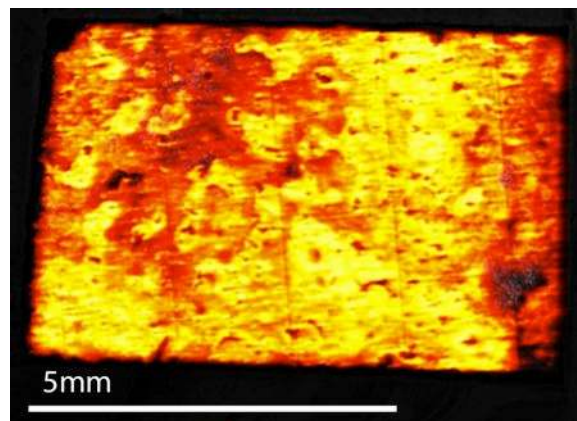
Fig. 6.   LBIC map of the solid-state device of Fig. 4. The illuminated area was used to calculate the device area.

V. CONCLUSION

Regenerative photoelectrochemical systems are a useful tool for characterizing highly structured semiconducting materials. We have demonstrated the use of this approach in the fabrication of flexible SiMW solar cells and have quantified the effect of each processing step on the photovoltaic performance of the device. The technique can directly be applied to other photovoltaic materials in various nanowire, nancone, nano-porous, or other highly structured architectures that are designed to increase the light trapping and carrier collection in next-generation photovoltaics.

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