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PAPER

Comparison between the electrical junction properties of H-terminated and methyl-terminated individual Si microwire/polymer assemblies for photoelectrochemical fuel production†

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The photoelectrical properties and stability of individual p-silicon (Si) microwire/polyethylenedioxythiophene/polystyrene sulfonate:Nafion/n-Si microwire structures, designed for use as arrays for solar fuel production, were investigated for both H-terminated and CH_3-terminated Si microwires. Using a tungsten probe method, the resistances of individual wires, as well as between individual wires and the conducting polymer, were measured *vs.* time. For the H-terminated samples, the n-Si/polymer contacts were initially rectifying, whereas p-Si microwire/polymer contacts were initially ohmic, but the resistance of both the n-Si and p-Si microwire/polymer contacts increased over time. In contrast, relatively stable, ohmic behavior was observed at the junctions between CH_3-terminated p-Si microwires and conducting polymers. CH_3-terminated n-Si microwire/polymer junctions demonstrated strongly rectifying behavior, attributable to the work function mismatch between the Si and polymer. Hence, a balance must be found between the improved stability of the junction electrical properties achieved by passivation, and the detrimental impact on the effective resistance associated with the additional rectification at CH_3-terminated n-Si microwire/polymer junctions. Nevertheless, the current system under study would produce a resistance drop of ~20 mV during operation under 100 mW cm^{-2} of Air Mass 1.5 illumination with high quantum yields for photocurrent production in a water-splitting device.

Broader context

Photoelectrosynthetic splitting of water to store solar energy in the simplest chemical bond, H–H, would provide a globally scalable means of compensating for the intermittency of solar energy at a given region of the earth's surface. A working device will require: a light harvesting component; redox catalysts; and a membrane barrier, for separating the products of the oxidation and reduction reactions, while maintaining efficient ionic conductivity to maintain charge neutrality. Given the useable solar energy range and the energy requirements for both oxidation and reduction reactions, it is challenging to find a single light absorber that can function efficiently. As in the natural photosynthetic system, it is possible to combine two light absorbers across a product-separating, ionically conductive membrane; however, the membrane is then required to manage, with minimal resistance, electron transport between the two light absorbers. We report herein the photoelectrical properties of a test structure of this type of device, incorporating an individual semiconductor photoanode and photocathode (with no redox catalysts) embedded into a candidate conducting polymer membrane, to form a single functional unit.

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† Electronic supplementary information (ESI) available: Metallic catalyst removal procedure, microwire methylation procedure, conductive polymer film preparation, microwire/polymer junction formation, resistance *vs.* probe spacing measurement results for CH_3-terminated microwires, Au contact/polymer junction I–V character, initial XPS analysis results for H-terminated and CH_3-terminated Si microwires over time. See DOI: 10.1039/c2ee23115h

I. Introduction

A membrane-bridged microwire structure (Fig. 1) is an interesting approach to the production of hydrogen using sunlight.[1–7] In this approach, two semiconductors functioning electrically in series would provide the necessary photovoltage (>1.23 V) to split water into $H_2(g)$ and $O_2(g)$. Suitable electrocatalysts would be used to drive the fuel-forming anodic and cathodic reactions at low overpotentials.[6,7] The membrane would support and incorporate the two semiconductor materials, and must also allow for ionic and electronic transport, to complete the circuit while separating the $H_2(g)$ and $O_2(g)$ with minimal product crossover.[8–10] One important aspect of this proposed device structure is the electrical behavior of the contacts between the semiconducting microwires and the conducting polymer.[3,11–14]

H-terminated Si microwires have relatively low surface recombination velocities, and can provide an approach to producing the photocathode portion of such a structure. H-terminated Si microwires have been used in solar cell,[15–18] organic,[19] liquid junction,[20,21] and inorganic solid-state[16] devices, as well as for photocathodes in photoelectrochemical H_2 production from water.[22] The electrical properties of Si microwires have been studied in contact with polyethylenedioxythiophene/polystyrene sulfonate (PEDOT:PSS):Nafion films, and in some cases the junctions have been shown to be ohmic and of acceptably low contact resistance to be useful in the proposed membrane structure. However, oxide formation within the Si microwire/conducting polymer membrane junction would significantly increase the junction resistance, resulting in electrical losses during operation.[23] Such losses could compromise the functionality of the device, considering the limited amount of photogenerated voltage available to drive the water-splitting reactions.[6,7,11,12,24]

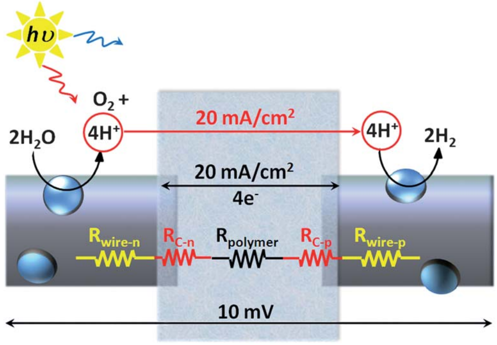

Fig. 1 Schematic diagram of a single unit cell of the proposed photoelectrochemical device. Each cell would ideally include two semiconductors with sufficiently large bandgaps to provide the necessary photovoltage for water splitting, and the semiconductors would have electrocatalysts deposited onto the wire surfaces. The semiconducting light absorbers (in this case Si microwires) would be embedded into an electronically and ionically conductive membrane. The various DC series resistances that contribute to the total resistance of the system are shown. R_{wire} and $R_{polymer}$ represent the microwire and polymer resistances, respectively, whereas $R_{C\text{-}n}$ and $R_{C\text{-}p}$ are the junction resistances of the n-Si and p-Si microwire/polymer contacts, respectively. The maximum acceptable photovoltage drop across the cell is 10 mV for 20 mA cm^{-2} of photocurrent density. Reprinted with permission from ref. 47. Copyright (2011) American Chemical Society.

One approach to prevent oxide formation is to chemically passivate the Si microwire surface through surface functionalization reactions that exploit the kinetic stability of the Si–C bond.[25–27] Alkylation of H-terminated Si using alkylmagnesium reagents;[28,29] radical halogenation;[30] chemical free-radical activation;[31,32] irradiation with ultraviolet light;[33–37] thermal activation;[32,38–40] and hydrosilylation[41–43] has been reported for both the Si(100)[39,44] and Si(111) surfaces,[23,26,45] as well as for porous Si.[46] In some cases, such surface functionalization has been shown to produce enhanced oxidative stability and to result in a low surface recombination velocity.[27]

We report herein the electrical behavior of the contact between a conducting organic polymer and functionalized Si microwires. Functionalization of Si microwires with methyl groups produces surfaces that are electrically and chemically stable, with negligible native oxide growth over time.[23,26,27,45] The CH_3-terminated Si microwires were used to form single microwire device structures that contain the main structural features involved with a membrane-supported photoelectrosynthetic device.[47] Although CH_3–Si termination is expected to suppress oxide formation, CH_3-functionalization of Si is also expected to produce an interfacial dipole that should result in a shift in the barrier height of the Si/polymer contact. Specifically, relative to H-terminated Si microwires, increased rectification is expected at CH_3-functionalized n-Si/polymer contacts and decreased rectification is expected at CH_3-functionalized p-Si/polymer contacts. In this work, we have directly compared the electrical properties of CH_3-terminated and H-terminated Si microwires with the same conducting polymer. The data include electrical parameters that cannot be precisely determined from bulk measurements, such as the Si microwire resistivity, the total series resistances in the microwire/conducting polymer system, and the stability over time of the wire/polymer junction.

II. Experimental

A. Si microwires

Si microwires were grown by vapor–liquid–solid (VLS) chemical vapor deposition (CVD) methods. The substrates were Si(111) wafers that were patterned photolithographically with Cu catalysts. During growth, the wires were doped with either boron (B) or phosphorus (P) to concentrations of 10^{17} to 10^{18} cm^{-3}.[13,20,48,49] The single crystalline Si microwires were 90 ± 15 μm in length, ~1.5 to 1.7 μm in diameter, and were arranged in a square pattern with a 7.0 μm pitch. Residual metallic growth catalyst at the top of each microwire (and some small amounts on the sides) was removed using a two-step etching procedure (ESI†). The microwires were terminated with methyl groups (ESI†) using a two-step chlorination–alkylation procedure.[26,27]

The microwires were removed from the growth substrate either by sonication[50] or by scraping a corner of the substrate using a razor blade. The microwires were suspended in isopropanol or acetonitrile, and a drop of the suspension was deposited onto the glass substrate to facilitate measurements on individual microwires. Prior to each set of measurements, surface oxides were removed by etching the Si microwires in buffered HF(aq.). The time interval between the oxide removal process and the measurements was typically <15 min.

To eliminate any variation in the results due to microwire growth variability, all the microwires were taken from a common set of growth runs. The microwire samples were divided into two separate batches, with the first batch etched in HF(aq.) to remove the native oxide, and the second batch methyl-terminated. The junction behavior of H-terminated and CH_3-terminated Si microwires was evaluated for Si microwires having either p- or n-type doping.

B. Conducting polymer films

Solutions of the conducting polymer, polyethylenedioxythiophene/polystyrene sulfonate/Nafion (PEDOT:PSS:Nafion) with 12 wt% PEDOT:PSS,[10] were prepared according to established procedures (ESI†). Conducting polymer films (thickness: 150 to 200 nm) were deposited by spin-coating a solution of polymer onto a glass substrate that contained prepositioned Parafilm masks on opposite ends of one side of the substrate, with the polymer film deposition forming a lane on the substrate. After removal of the Parafilm mask, p-type or n-type Si microwires were deposited onto the exposed glass substrate. Using tungsten probes, single microwires were then positioned perpendicular to the border between the conducting polymer and the glass substrate. To ensure good electrical contact between the polymer and the microwire, approximately 2–5 μm of the microwire length that was in contact with polymer was covered with a small amount (<10 μL) of polymer. Ohmic contacts to the conducting polymer films were then formed by sputtering 32 nm thick pads of Au directly onto the polymer. This p-Si microwire/polymer/n-Si microwire assembly (Fig. 2) was used as a model for a single unit of the proposed solar water splitting microwire array cell (Fig. 1).

C. Instrumentation

Following the preparation of polymer membranes, an Edwards s150b sputter coater was used to sputter Au pads onto the polymer surface. A Fogale Photomap 3D optical profilometer and a KLA Tencor AS-500 Alpha-Step were used for the polymer film thickness measurements. X-ray photoelectron spectroscopic (XPS) analysis on the microwire samples was performed using a Kratos Axis Ultra DLD instrument. Current *versus* voltage (*I–V*) measurements were performed in a standard probe station using an Agilent 4155c semiconductor parameter analyzer. A Newport model 96000 full spectrum solar source with a global Air Mass (AM) 1.5G filter was used to simulate the standard solar irradiance spectrum. Tungsten probes (with a diameter of ∼1 μm), used in the *I–V* measurements, were etched for ∼30 s in 2.0 M KOH(aq.) immediately before the experiments, to remove the tungsten native oxide and to improve the quality of the contacts.

III. Results

A. Single microwire measurements

The doping concentration *vs.* distance along the Si microwires was investigated through resistance measurements (ESI†)

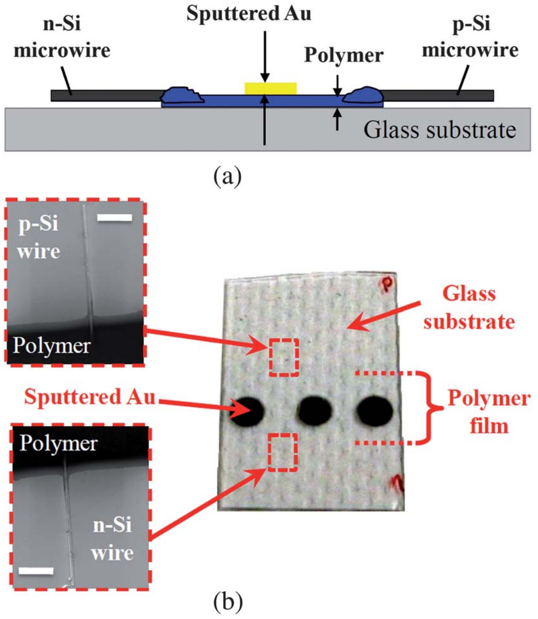

Fig. 2 (a) Schematic diagram of the measurement system. This system was used as a representation for the photoelectrochemical device depicted in Fig. 1. The PEDOT:PSS:Nafion film (∼200 nm thick) was spin-coated onto a glass substrate. H-terminated and CH_3-terminated p-type and n-type Si microwires were aligned at the polymer/glass border, with 2–5 μm of the microwire embedded into the polymer. Au contacts (32 nm thick) were sputtered onto the polymer to provide ohmic contacts to the polymer membrane; (b) photograph of the test structure, along with SEM micrographs of the microwires aligned at each side. SEM images were taken on a gold-coated slide to minimize charging issues. The scale bars in the images are 20 μm.

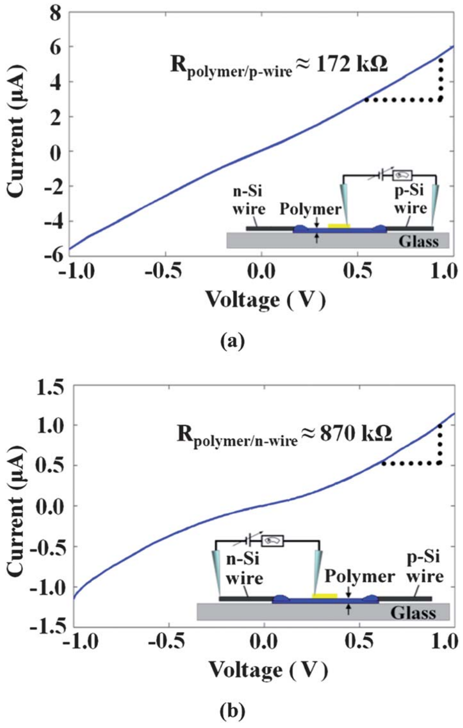

Fig. 3 *I–V* data for a 100 μm long freshly etched (a) H-terminated p-type Si microwire and (b) H-terminated n-type Si microwire, both with diameters of ∼1.5 μm aligned at the PEDOT:PSS:Nafion/glass border (figure insets). The total series resistance of the system in each case (displayed in the figures) was used to extract the junction resistance, $R_{C\text{-}p}$ or $R_{C\text{-}n}$, by incorporating the known values of R_{wire} and $R_{polymer}$.

obtained using a direct-contact technique.[14,47] The resistance per unit length of the CH_3-terminated microwires was ~0.50 kΩ μm^{-1} and 0.18 kΩ μm^{-1} for the p-type and n-type Si microwires, respectively. As expected, these values are similar to those reported for H-terminated Si microwires.[47] The contact resistance between the tungsten probes and the microwires was also calculated by performing a linear fit to the resistance *versus* probe separation data,[14,47] and was verified to be a negligible contribution (<1 kΩ) to the total measured resistance for the system. The doping concentration of the microwires was uniform over the length scales considered, and was estimated to be 10^{17} to 10^{18} cm^{-3}, well within the expected range of doping concentrations based on the growth conditions.[13,20,48,51]

B. Single Si microwire/PEDOT:PSS:Nafion system

Using the tungsten probes, the microwires were aligned on the polymer films (Fig. 2b). The sputtered gold/polymer junction exhibited well-defined ohmic behavior (ESI†), and the tungsten probe/microwire junction also demonstrated ohmic character, with negligible contact resistance when compared to the other resistances in the system. To extract the contact resistance between each type of Si microwire and conducting polymer, the current that passed through the system for different applied voltages was recorded with one tungsten probe in contact with the microwire, while the other probe was placed on the gold contact (insets of Fig. 3). The total measured resistance included contributions from the conducting polymer, $R_{polymer}$ (measured using a 4-point probe technique), the microwire/polymer contact, R_C (denoted as $R_{C\text{-}p}$ for p-type microwires and $R_{C\text{-}n}$ for n-type microwires), and the microwire, R_{wire} (denoted as $R_{p\text{-}wire}$ for p-type and $R_{n\text{-}wire}$ for n-type microwires, measured as described in Section A). The microwire/polymer contact resistance was then calculated from the total measured series resistance by incorporating the known values (R_{wire}, $R_{polymer}$).[14]

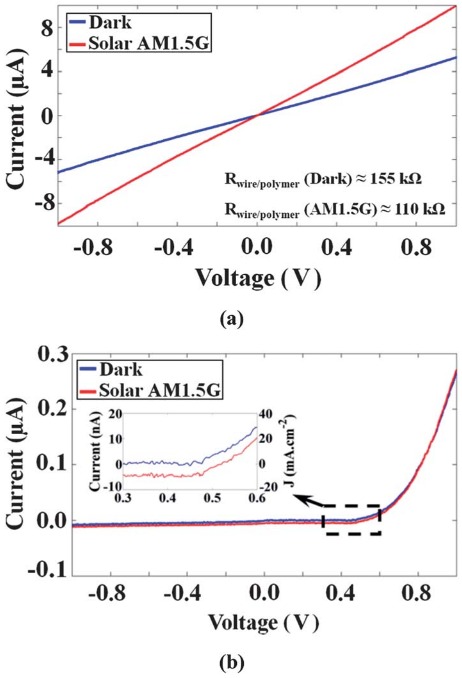

Fig. 4 Measured *I–V* data for a 100 μm long CH_3-terminated (a) p-type and (b) n-type Si microwire with a diameter ≈ 1.5 μm aligned at the PEDOT:PSS:Nafion/glass border, in dark and under solar AM 1.5G illumination. As expected, ohmic behavior was observed at the p-Si microwire/polymer contact. A strong rectifying behavior was observed at the CH_3-terminated n-Si microwire/polymer junction.

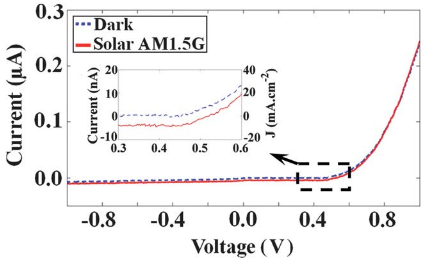

Fig. 5 Measured *I–V* response for a complete photoelectrosynthetic water splitting cell with ~100 μm long CH_3-terminated p-Si and n-Si microwires with diameters of ~1.5 μm. The electrical character of the cell is dominated by the rectifying behavior at the CH_3-terminated n-type microwire/polymer junction.

The *I–V* data for H-terminated Si microwires aligned at the PEDOT:PSS:Nafion/glass border (Fig. 3) indicated ohmic behavior at the junction between H-terminated p-Si microwires and the PEDOT:PSS:Nafion and non-ohmic behavior between H-terminated n-Si microwires and the polymer.

CH_3-terminated p-Si microwires aligned at the polymer/glass border exhibited ohmic character (Fig. 4a), in agreement with prior measurements on planar CH_3-terminated p-Si and PEDOT.[7] Fig. 4b shows the junction properties of CH_3-terminated n-Si microwire/polymer junctions, demonstrating rectifying behavior (Fig. 4b) and in effect showing a large junction resistance. After one month under laboratory conditions, such samples exhibited less than 10% increase in the junction resistance. This behaviour verifies the stability of these junctions as compared to the H-terminated samples which demonstrated a more than 20-fold increase in the junction resistance under the same conditions. Under 1 Sun illumination (AM1.5G, 100 $mW.cm^{-2}$) an increased conductivity was observed in the p-Si microwires (Fig. 4a), leading to a slightly lower $R_{wire/polymer}$ value. In these measurements, microwires were lying flat on the substrate, as indicated in Fig. 2, and were illuminated from above, so the illuminated photoactive area was ~1.5 μm × 100 μm.

The electrical character of the model water-splitting cell, formed using the combination of CH_3-terminated n-Si and p-Si microwires bridged by the PEDOT:PSS:Nafion conductive polymer, was dominated by the rectifying behavior at the n-type microwire/polymer junction (Fig. 5). Under illumination, ~5 nA of short circuit current was measured for this rectifying junction and in the conduction region, the dark and illuminated resistance values were nearly identical. Table 1 summarizes the measured resistances for both H-terminated and CH_3-terminated samples.

IV. Discussion

Conventional approaches to form ohmic contacts to individual Si microwires (*e.g.* thermal evaporation of contact metals)[50,52,53] are only applicable to a certain range of microwire diameters, and are not compatible with many microwire/polymer structures, due to the complexity of the interactions between

Table 1 Measured resistances (±1%) for both H-terminated and CH_3-terminated Si microwire/polymer systems. The microwire length and diameters were ∼100 μm and ∼1.5 μm, respectively. In the case of rectifying junctions, the measured resistance represents the series resistance in the turn-on region

R (kΩ) ± 1%	$R_{\text{wire-p}}$	$R_{\text{wire-n}}$	$R_{\text{C-p}}$	$R_{\text{C-n}}$	$R_{\text{PEDOT:Nafion}}$	Expected R_{total}
H-terminated (dark)	50	18	∼120	∼850	2	1040
CH_3-terminated (dark)	50	18	∼100	∼900	2	1070
CH_3-terminated (Solar AM1.5G)	∼30	∼10	∼90	∼850	2	980

polymers, photoresists, and the etchant solutions, as well as the high temperatures used during lithographic processes. Previous reports have demonstrated that with the application of sufficient local mechanical pressure, direct and reliable ohmic contacts to the Si microwires can be made by the use of tungsten probes.[14] The method also enables the basic electrical properties of single Si microwires and of Si microwire/polymer junctions to be extracted in a standard probe station, without the need to thermally evaporate metallic contacts.[14,47]

The characteristics of the n-type Si microwire/polymer junction can be ascribed to a work-function mismatch between the n-type microwires and PEDOT:PSS:Nafion film, which has p-type characteristics.[54,55] Methylation of Si shifts the energetics of the Si band edges by creation of negative dipoles at the surface,[6,26,27] inducing an increased barrier height at the n-Si microwire/polymer junction. Approximately 500 mV is required to overcome this energy barrier, as indicated in Fig. 4b. Consistently, methylation produced lower resistance, more ohmic, contacts between p-Si microwires and PEDOT:PSS:Nafion films.

Although the H-terminated Si microwires were etched immediately prior to the measurements, a thin layer of native oxide likely formed on the surface of the Si, because the alignment of the microwires at the polymer–glass interface was conducted in air. Quantum mechanical tunneling through the native oxide is thus expected to contribute to the nonlinearity in the *I–V* profile of the H-terminated Si microwire/polymer junctions. Consistently, *I–V* measurements performed after aging of the H-terminated microwire/polymer junctions for a month in air revealed a more than 20-fold increase in the junction resistance, and in some cases loss of electrical conduction at the junction, presumably reflecting the deleterious effects of increased oxide formation on the Si surface.

The increase in the junction resistance with time for CH_3-terminated microwires is potentially due to oxidation of the backsides of the microwires where they had been cut off from the growth substrate. However, as confirmed by XPS measurements, CH_3-terminated n-Si microwires showed significantly improved oxidative stability (ESI†) compared to the H-terminated microwires.

Absorption of all above-bandgap photons incident normal to a 7 μm pitch size microwire array at 100 mW cm^{-2} (the global AM 1.5 spectrum) should result in a maximum of ∼21 nA short-circuit photocurrent in each microwire.[14,56] To minimize the impact of iR losses in a functional system, voltage drops of <∼10 mV would produce losses that were ∼1% of total photogenerated voltage required for water splitting. Assuming a current of 21 nA flowing through the junction to the polymer film, the maximum acceptable resistance to produce a 10 mV voltage drop in the microwire–polymer system is ∼480 kΩ. Hence, the p-Si microwire PEDOT:PSS:Nafion contacts meet this criterion, whereas n-Si microwire PEDOT:PSS:Nafion contacts exceed this target voltage drop by a factor of ∼2 (Table 1).

Fully ohmic behavior across all inner contact junctions in such a model water-splitting cell could be achieved by combining two separate conducting polymers, one that makes ohmic contact to each electrode. Alternatively, increased junction conductance would be expected from modification of the n-type microwire base (in contact with the membrane), either by addition of a metallic interfacial layer or by increased doping (degenerate levels) to narrow down the depletion region and facilitate quantum mechanical tunneling of charge carriers.[57]

V. Conclusions

The electrical properties of a single cell of a proposed photoelectrosynthetic fuel production system, as well as of each junction within the cell, were investigated both in the dark and under simulated 1 Sun AM 1.5G illumination. H-terminated Si microwire/polymer contacts exhibited poor long-term stability, whereas CH_3-terminated Si microwires demonstrated increased stability toward oxidation behavior as compared to their H-terminated counterparts. CH_3-terminated p-Si microwires yielded ohmic contacts at PEDOT:PSS:Nafion junctions, whereas CH_3-terminated n-Si microwire/PEDOT:PSS:Nafion junctions demonstrated rectifying behavior, potentially due to the shift in the energy of the Si band edges at the interface, induced by creation of a surface dipole.

Acknowledgements

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