5 Magnetically Aligned Silicon Microwire Array Devices

The magnetic alignment of silicon microwires from random solution into vertically oriented ensembles on the centimeter scale has been demonstrated and characterized previously. These vertically oriented films have the potential to function as solar absorber layers in photoelectrochemical or photovoltaic devices. Previous microwire array-based solar cell devices have incorporated microwire elements grown using conventional chemical vapor deposition and photolithographic techniques and are therefore potentially less scalable. A device design leveraging scalable magnetically aligned films is presented here and compared to conventional microwire array designs.

5.1 Background and Introduction

It has been shown that ensembles of 100 μm long Si microwires coated with ferromagnetic Ni layers can be vertically oriented in the presence of an approximately 300 G magnetic field, with the exact field dependent upon the geometric and surface energetic parameters of the given system. [1] These films can be subsequently captured in a flexible polymer film for use as solar absorber layers, and the ferromagnetic handle removed to allow for increased light absorption. This process is scalable and uses only solution-based processing methods. Additionally, it can be generalized to a wide range of devices where the preferential orientation of an array of nano- or microscaled components is necessary and desired.

Previous work has shown that microwire array devices can be used to fabricate high efficiency devices, both photoelectrochemical [6] and photovoltaic. [5] These devices use polymer encapsulated Si microwire films that have been removed from the growth substrate, where they were grown using conventional chemical vapor deposition techniques. [43] It should therefore be possible to use parallel processing techniques to render a magnetically aligned and polymer encapsulated microwire film into a similar device. As a control, a solution of microwires was prepared by randomizing an array of substrate grown wires, and following magnetic alignment the resulting array was compared to the previously cite literature cells.

The vertical orientation of the wires has been characterized by X-ray diffraction (Figure 5, Section 3.2.3) as having 97% of the integrated area within $\pm 5°$, which is comparable to orientation of wires pulled directly off a single crystal growth substrate. [43] This degree of orientation is independent of aligned film density. The average density of the magnetically oriented arrays using standard parameters however is approximately 80 mm^{-2} (Section 3.2.2). This can be increased to a maximum

of about an order of magnitude higher by orienting a fully close packed horizontal monolayer. By comparison, arrays grown on the substrate have a density of approximately 20,000 mm^{-2}. While scattering elements or slantingly aligned arrays can be used to mitigate the loss of light absorption through incomplete areal coverage of Si, [5,58] this two to three order of magnitude difference in density would likely result in a large loss of photocurrent. A method for the densification of arrays produced through directed assembly is therefore necessary. Two methods for array densification will be discussed, followed by a proposed device construction scheme.

5.2 Densification of Magnetically Aligned Arrays

Two methods have been investigated for the densification of vertically aligned arrays, with the aim of increasing overall array density by a factor of 100 to 1000. The first method involves a densification step after the magnetic alignment using an elastomeric alignment substrate and the second involves use of a specially designed cell to vertically deposit wires in a denser array than would be possible using the two step horizontal deposition followed by magnetic alignment process discussed throughout Section 3.

5.2.1 Elastomeric Densification

The magnetic alignment process is largely substrate agnostic, so long as a sufficient magnetic field can be applied corresponding to the interaction between the substrate, the solvent, and the wire. This allows the use of unusual substrates such as polymers in place of smooth crystalline surfaces. It has been shown previously that by dispersing wires horizontally on a pre-strained polymer layer that the ensemble of wires becomes more dense following the relaxation of the substrate strain. [59] A two-axis stretching device was fabricated in order to test microwire alignment on strained substrates (Figure 19).

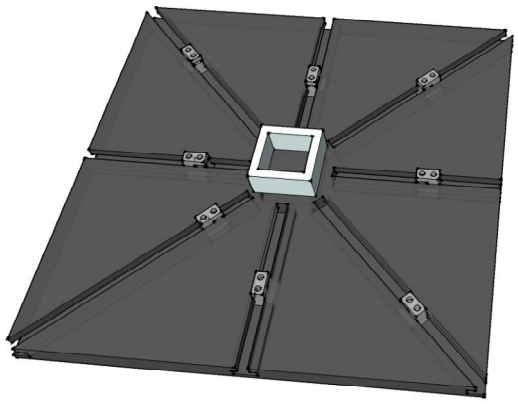

Figure 19: Schematic of two-axis elastomeric alignment device. The gray blocks pin the substrate to various strains and the center pit confines the deposition solution to the substrate.

Using this device and the appropriate choice of elastomeric substrate it is possible to have a several times compression in each of the two dimensions. A one-axis elastomeric alignment is shown through dark-field optical micrographs in Figure 20 below, where a solution of Ni-plated Si microwires was dropcast onto a Neoprene substrate.

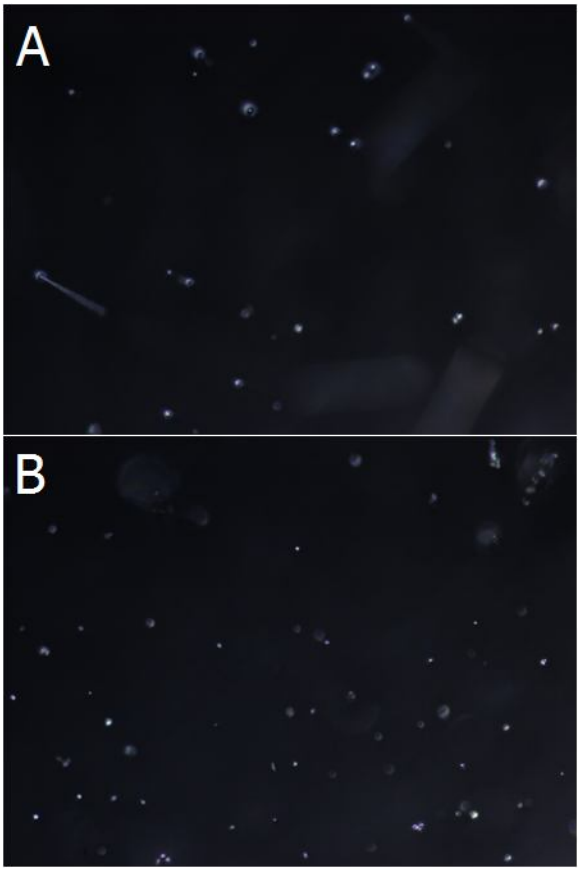

Figure 20: Dark-field optical micrographs of an elastomeric densification of Si microwires. (A) A 2.25× strained Neoprene substrate. (B) The densified ensemble following strain release.

The result is that a 2.25 × strain along one axis of the substrate prior to deposition and alignment leads to a corresponding increase in the density of the array in that axis. This is a relatively facile process that has the added advantage that the movement of the polymer under the microwires influences them to align at lower applied fields due to the breaking of the van der Waals interaction between the microwires

and the substrate. This can be seen by in Figure 20, where some of the wires were horizontal in panel A, but all had aligned by the image in panel B. Nonetheless, with common elastomer choices the maximum compression allowed is approximately 25 × which is insufficient densification for high-quality devices.

5.2.2 Flow Cell Alignment

A second method was explored for increasing the density of a microwire array which involved aligned deposition of the microwires as opposed to alignment following deposition. A scheme of the process is given in Figure 21 below.

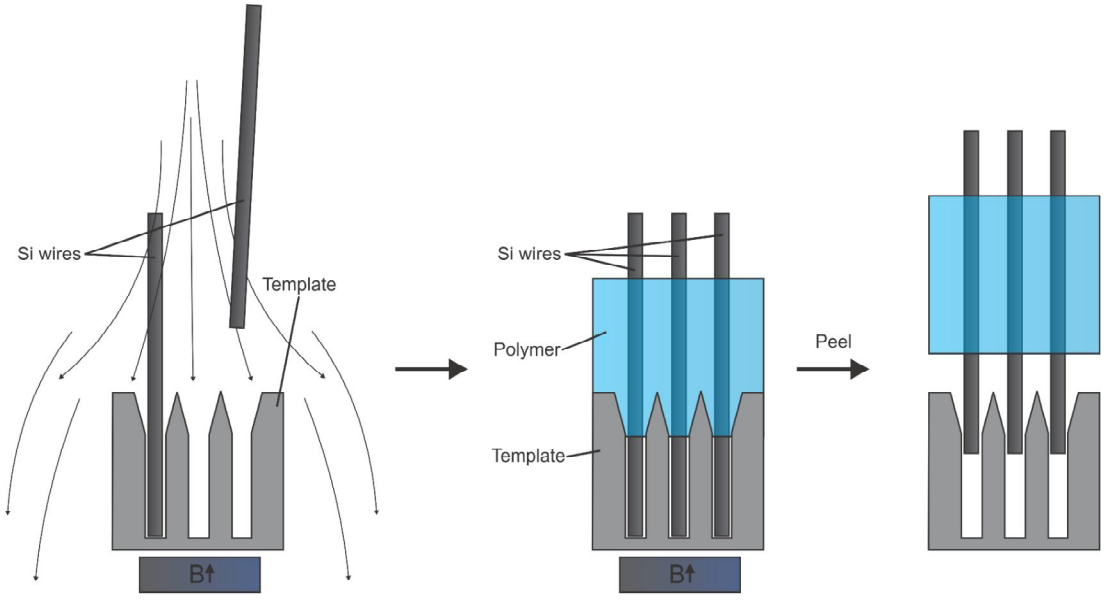

Figure 21: Schematic showing the process of aligning microwires under a magnetic field into a pre-patterned template using a jet of microwire solution, followed by microwire array removal in a polymer film.

In the first step a jet of microwire-containing solution is projected over the top of a templated substrate with pores matching the microwire diameter and pitch matching the desired pitch for the aligned film. A magnetic field is applied so the microwires remain parallel to the axis of the pores. By recirculating the solution the template can be filled completely. In the second step a polymer film is cast around the top halves

of the microwires and cured. This allows for the third step where the microwires are removed from the template using the polymer film as a mechanical support, regenerating the template for further use. Due to this, while the fabrication of the template itself is energy-intensive, the overall cost is low when it can be reused indefinitely.

The flow cell used in this study is shown schematically below in Figure 22. Left is shown the cell itself, with a recirculating pump, magnetic pedestal, and the alignment template affixed to the pedestal. In addition, the inlet jet has an electromagnetic coil wrapped around the barrell. The inset to the right shows an electron micrograph of the alignment template. The alignment template is macroporous Si prepared from planar Si *via* anodic etching in an ethanolic solution of hydrofluoric acid (1:2:3 buffered hydrofluoric acid, ethanol, and deionized water by volume) for 60 min at a constant current of 11.5 mA cm^{-2}. [60–62]

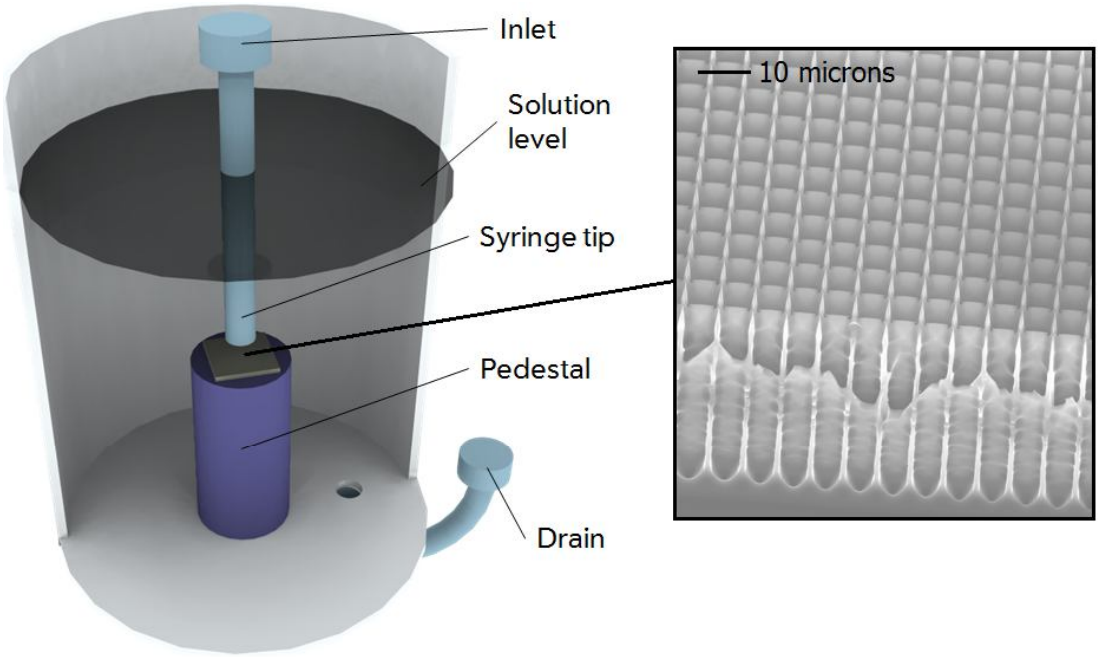

Figure 22: Schematic illustrating the flow cell used for magnetic alignment into a pre-patterned template (shown in electron micrograph) using a jet of microwire solution.

Microwire arrays prepared through the use of the cell in Figure 22 are presented in Figure 23, with a plan view optical micrograph in panel A and an electron micrograph cross-sectional view in panel B. The arrays in these micrographs show good vertical alignment and are suitable for characterization by the methods discussed in Section 3.5.3. X-ray diffraction data for the array in panel B is given in Figure 5.

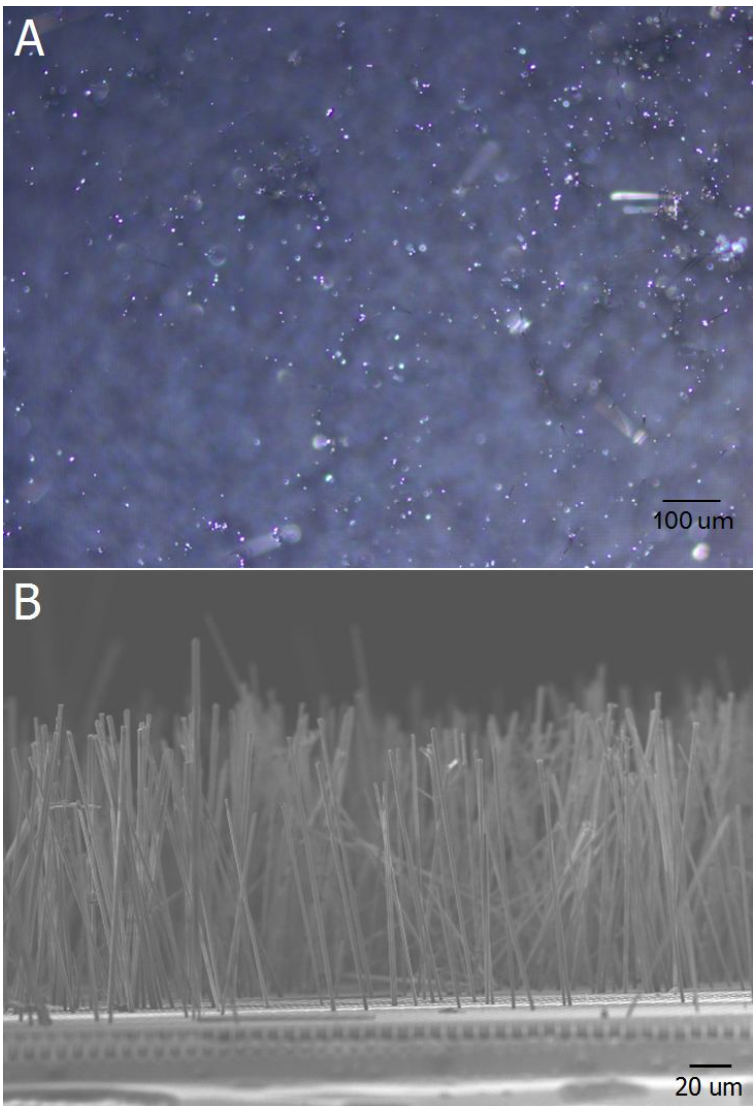

Figure 23: Micrographs of microwire arrays prepared *via* flow cell magnetic alignment. (A) Optical micrograph plan view of vertically aligned array. (B) Electron micrograph cross-sectional view of microwire array.

The microwire arrays prepared here can be extracted from the template using a polymer infill process, where the array is peeled off following the cure of the polymer, resulting in a flexible, free-standing array. In this case, the wires were extracted for the template using polydimethylsiloxane (PDMS), an inexpensive, inert, insulating polymer. The template was rendered hydrophobic *via* vapor phase silanization for 5 min in a sealed vessel with perfluorododecasilane (Gelest, used as received) prior to the magnetic alignment process. The polymer was partially cured for approximately 5 min at 120 °C and the templated array placed upside-down on the polymer layer, allowing the ends of the wires to sink into the PDMS. The sample was cured a further 20–30 min at 120 °C and the PDMS peeled from the template, resulting in a free-standing layer.

5.3 Photoelectrochemical Device Fabrication

Photoelectrochemical cells are an excellent way to characterize the properties of semiconducting light absorbers. By making rectifying contact to the semiconductor through a solution redox couple it eliminates the need to make a solid-state p–n junction. Additionally, liquid contacts are by their nature conformal which makes them ideally suited to studying high-aspect ratio structures like microwire arrays. Conventionally grown microwire arrays have been studied in non-aqueous conditions in with ferrocene/ferrocenium as the redox couple [63] and in aqueous conditions using methyl viologen. [6] Photosynthetic cells with attached catalysts have been studied as well for the production of H_2. [64, 65]

5.3.1 Proposed Fabrication Scheme

The proposed fabrication scheme culminating in a cell suitable for liquid junction characterization is shown below in Figure 24. In panel A microwires are prepared, either by solution growth or by conventional CVD processes for control samples. The microwires are plated with Ni, by electroless deposition using Ni electroless deposition solution (Transene, used as received), or electrodeposition from Ni sulfamate solution (Transene, used as received) at -1 V for 10 min in the case of control samples. In panel B the microwires are detached from the substrate (if necessary) and evenly dispersed on a planar substrate. Steps A and B have been well explored and are described in Sections 3 and 4. Alternatively, the wires can be deposited in a magnetic alignment flow cells as described in Section 5.2.2. In panel C the microwires are magnetically aligned (or embedded in) a polymer solution containing PEDOT:PSS and Nafion, a known conductive polymer blend. [66] In panel D the conductive polymer is cured by the application of heat or time and the magnetic field removed. In panel E the top half of the Ni shell is etched off to expose the underlying Si to solution. The etchant used is known as the RCA2 process and comprises exposure to a

5:1:1 H_2O:HCl:H_2O_2 solution at 80 °C for 10 min. In panel F a PDMS buffer layer is cast to isolate the conductive polymer layer from solution, thereby preventing shunt currents. In panel G a layer of Ag $\sim$100 nm thick is sputtered to serve as a metallic back contact. In panel H the cell is submerged in solution to study its properties photoelectrochemically. A solution of the methyl viologen$^{2+/+}$ redox couple would be used as described previously. [6]

One modification to this procedure would be to omit the conductive polymer step in place of a thicker PDMS layer. This would assume that the sputtered Ag is able to make appropriate ohmic contact through the bases of the wires, rather than the entire bottom section as would be contacted with the scheme as originally proposed.

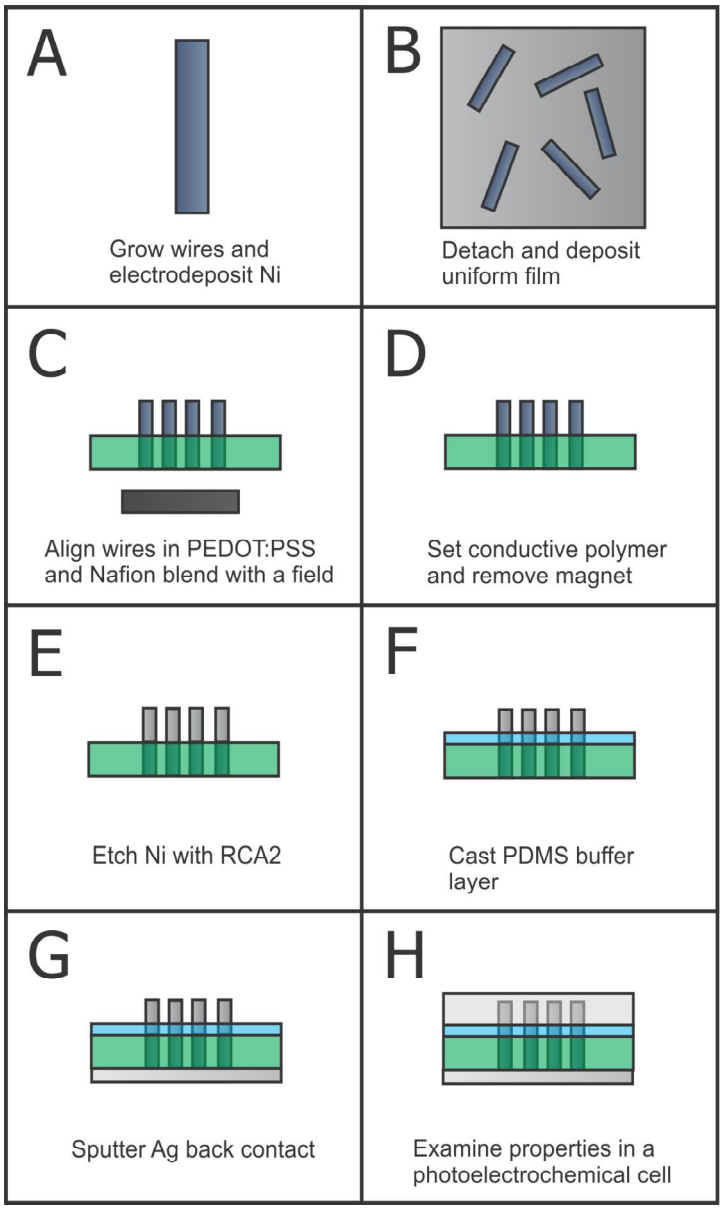

Figure 24: Device scheme for fabrication of magnetically aligned photoelectrochemical cell. (A) Wires are grown *via* conventional or solution phase methods and plated with Ni using either electro- or electroless deposition. (B) The wires are detached (if necessary) and dispersed evenly on a flat substrate. (C) The wires are magnetically aligned in a polymer solution comprised of a blend of PEDOT:PSS and Nafion. (D) The polymer is cured and the field removed. (E) Ni is etched from the top half of the wires using the RCA2 process. (F) A PDMS buffer layer is cast to isolate the back contact from solution. (G) A film of Ag is sputtered as the back contact. (H) The cell is immersed in solution for photoelectrochemical testing.

5.3.2 Characterization Results

The electrical contact scheme was tested in a planar configuration as shown in Figure 25. In this test device a chip of p-Si with resistivity of 0.1 Ω cm was used to emulate the microwire array. This resistivity matched the measured values of resistivity measured from as-grown microwires using single wire photolithographic contacting methods. [67] A layer of Ni ($\sim$300 nm) was electrodeposited as described previously, with a center channel masked off to provide electrical isolation. An island of PEDOT:PSS Nafion blend was dropcast on one of the Ni contacts. Finally, an island of Ag ($\sim$100 nm) was sputtered on top of the polymer layer. Contact to the device is made for the Ag contact to the opposite Ni contact, resulting in a Ni–Si–Ni–PEDOT:PSS–Ag device, where the first Ni–Si junction takes the place of the Si liquid contact in the final proposed microwire device. If the conductive polymer layer provides a good ohmic back contact, the whole device should read as ohmic due to the second contact being an ohmic Ni–Si junction.

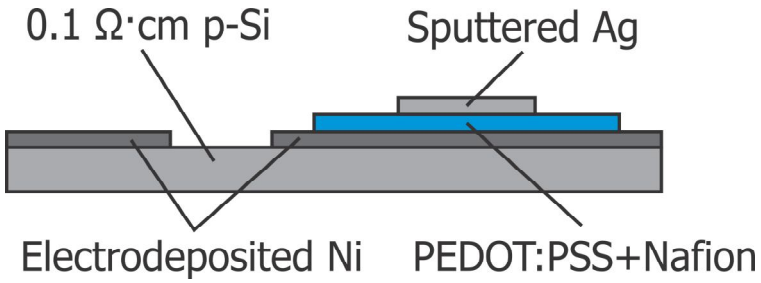

Figure 25: Schematic of planar test device for measuring the quality of the ohmic back contact to Si.

The results of the electrical testing of the device in Figure 25 are shown in Figure 26. Both the test sample and a control sample with two indium tin oxide (ITO), a commonly used transparent conducting oxide, pads are measured for their contact quality to p-Si. In both cases the samples show ohmic contact, reflected in the equal current passage at positive or negative bias voltage. The conductive polymer-based sample

in fact shows approximately an order of magnitude higher current passage demonstrating that the ohmic contact is of good quality.

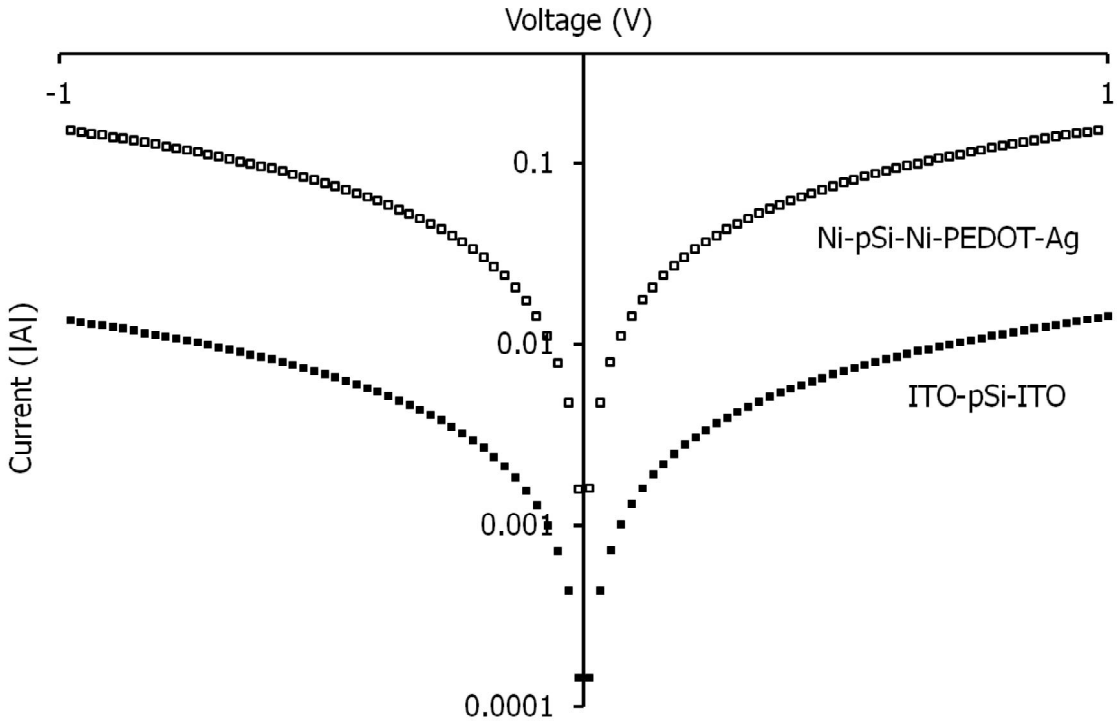

Figure 26: Current voltage behavior of the planar control sample shown schematically in Figure 25, along with the behavior of a ITO test device.

5.4 Conclusions

It has been shown that Si microwires can be vertically oriented in the presence of a magnetic field. This work further shows that alternative processes, namely elastomeric alignment and flow cell alignment can be used to increase the density of magnetically aligned films. Finally, a device architecture has been proposed for the testing of a flexible, free-standing, microwire array magnetically aligned and embedded in a polymer matrix. Methods for both the extraction of a polymer embedded array from the its template and a ohmic back contact using conductive polymers have been tested successfully. Future work will involve bringing these techniques together to form an actual microwire array device, and testing its performance photoelectrochemically against previous literature results for microwire array cells. If successful, this work has the promise to enable scalable, cost effective production of array-based solar devices.