Utilizing Solution-Grown Silicon Nanowires in Photovoltaic Devices

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Abstract and Introduction:

Photovoltaic (PV) devices were fabricated using solution-grown silicon nanowires and phenyl-C61-butyric acid methyl ester (PCBM). Silicon nanowires (SiNWs) were synthesized in relatively large quantities using the supercritical fluid-liquid-solid (SFLS) approach. Gold nanocrystals were used to seed nanowire growth and monophenylsilane (MPS) was used as the Si precursor. Devices were fabricated on glass substrates using a device architecture typical for bulk heterojunction PV device with a back contact of aluminum, an active layer of SiNWs and PCBM, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as the hole-transport layer, and a top contact of indium tin oxide (ITO).

Relatively low photovoltaic power conversion efficiency (PCE) under AM 1.5 illumination of 0.002% has been achieved to date. Several approaches were explored to improve device performance, including varying the weight ratio of SiNWs and PCBM, etching and redispersing the SiNWs prior to deposition, alternative spin coating methods, as well as chemical etching of the nanowire surface prior to device fabrication.

Methods:

SiNW synthesis was carried out using the system shown in Figure 1. The small piston and reactor were brought into the glove box and closed off. Reactant solutions of 0.5 ml MPS and 1.2 mg gold nanocrystals were loaded into the small piston followed by toluene to eliminate the remaining void space. The reactor was placed in a heating block with a Variac temperature controller and heated to 490°C. The inlet and outlet line to the reactor were purged while the six-way valve was under load mode. The reactor was then pressurized to 9 MPa and the six-way valve was changed to deliver mode. The remaining lines were purged of air and the inlet line to the small piston was attached. The reactor was then brought to 10 MPa and the flow dropped to 0.5 ml/min. SFLS growth within the reactor: MPS degrades into liquid silicon, in the supercritical region, which then bombards the gold nanocrystals, once completely saturated any additional silicon will generate the nanowire (Figure 2) from the gold seed [1].

An aqua regia etch was performed on some SiNWs prior to device fabrication. A 3:1 mixture of hydrochloric (10 ml) and nitric acid (3 ml) was achieved and placed on a stirrer. 10 mg of SiNWs were then dispersed in 20 ml of chloroform and added to the mixture. The stir speed was increased to obtain emulsion and the mixture was left covered for 4 h. The wires were cleaned several times using a centrifuge

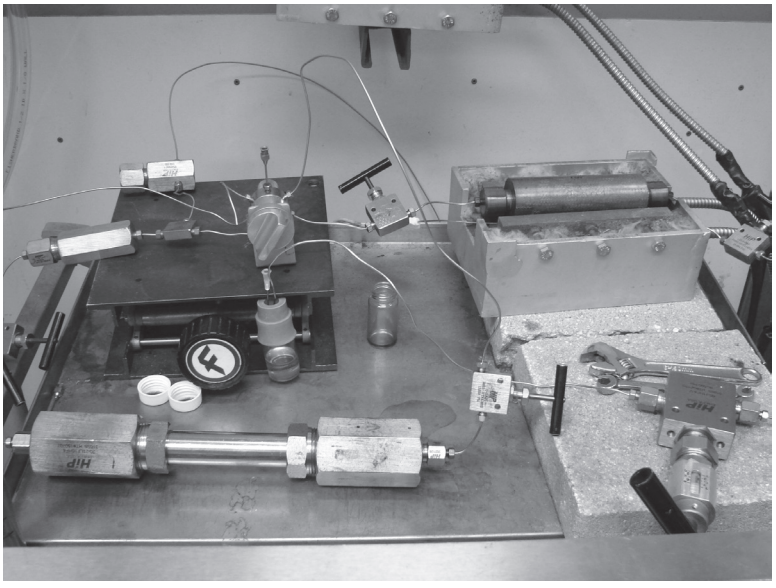


Figure 1: System used for SiNW synthesis.

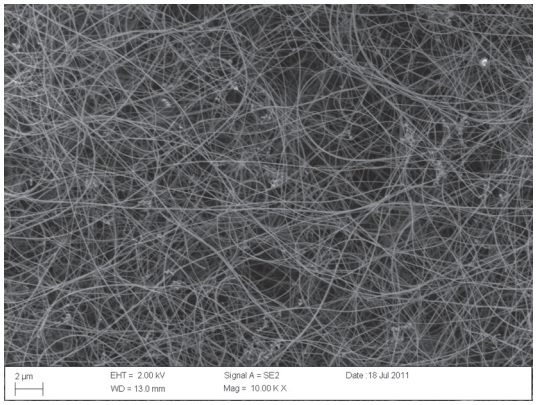


Figure 2: SEM image of SiNWs.

and redispersed in 20 ml of chloroform. Immediately following cleanup, the HF etch was completed. The wires were added to a 1:1:1 mixture of water, ethanol, and HF on the stirrer. The stir speed was again increased to obtain emulsion and the mixture was left for 15 minutes. The etch was followed by cleaning the wires and redispersing them in either chloroform, isopropanol, or 1,2-dichlorobenzene and quickly moved into an oxygen free environment.

Devices were fabricated on glass substrates covered with ITO and patterned using Kapton® tape and an Oxford plasma etch. The substrates were cleaned in consecutive five minute baths of acetone, isopropanol and water followed by 10 minutes in the UV ozone. PEDOT:PSS was then spin-coated onto the substrate at 5000 rpm. A mixture of PCBM and MPS SiNWs was then made to a desired weight ratio. The mixture was then injected onto the substrate and spun up to 600 rpm. After drying, the aluminum back contact was then deposited onto the substrate using a shadow mask and a Denton thermal evaporator. Silver paint was then painted on top of the aluminum contacts to help the card reader on the solar simulator.

Discussion and Results:

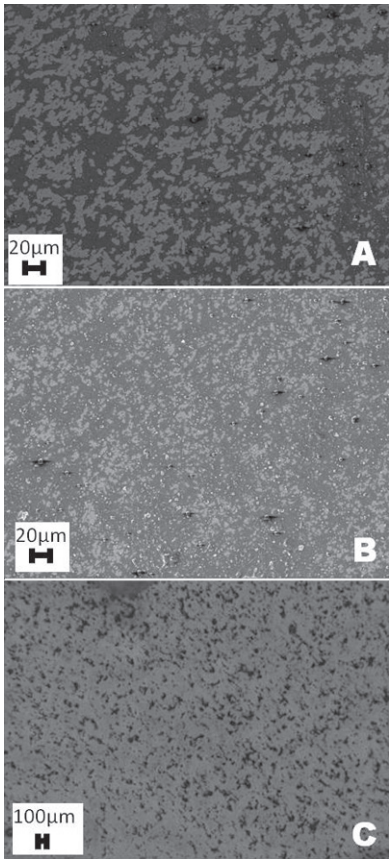
Figure 3 shows scanning electron microscopy (SEM) images of the average coverage of three devices. The gray area is PEDOT:PSS, while the darker areas in the images are composed of PCBM and SiNWs. The active layer of the devices was spin-coated in one of two methods: 1) injecting the PCBM/SiNW mixture once the substrate was spinning at 500 rpm, or 2) injecting the mixture while the substrate was stationary and then spinning it up to the desired speed. Figures 3a and 3b show SEM images for these two methods using non-etched SiNWs redispersed in chloroform. The second method shows an increased coverage of the active layer. Figure 3c shows the coverage of the active layer using the second method for spin coating and etched SiNWs redispersed in isopropanol. The coverage is greatly reduced from the non-etched SiNW devices however a PV response was seen after testing with a solar simulator. Figure 4 shows the current-voltage characteristics for this PV. The PCE of the device is 0.002%. The low PCE is most likely due to the non-uniform coverage of the nanowires.

Future Work:

In the future, we hope to prove hydrogen termination of the SiNWs post HF etch to ensure that oxygen is not interfering with current transfer. Although the etched SiNWs dispersed relatively well post etch in 1,2-dichlorobenzene, another option to enhance dispersibility could include functionalizing the wires with something that would increase dispersibility in dichlorobenzene. Device coverage might be improved by new spray coating methods or drop casting.

Acknowledgements:

Dr. Brian Korgel, Chet Steinhagen, Catherine Shipman and the remainder of the Korgel Group as well as the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, the National Science Foundation, the Robert A. Welch Foundation, Texas Materials Institute and the Center for Nano- and Molecular Science.



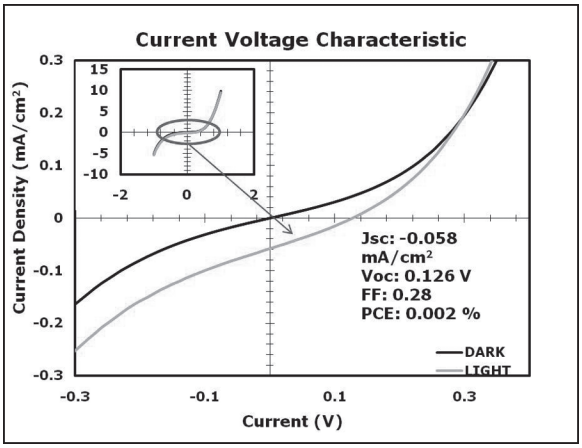


Figure 3, left: A. 6 weight percent (wt%) SiNW in PCBM spin coat method 1. B. 6 wt% SiNW in PCBM spin coat method 2. C. 6.5 wt% etched SiNWs spin coat method 2.

Figure 4, above: PV response from etched SiNW device.

References:

[1] Hanrath, T. and Korgel, B.A., Supercritical fluid-liquid-solid synthesis of Si and Ge nanowires seeded by colloidal metal nanocrystals. AdvMats (2003), 15(5), 437-440.