SILICON NANOWIRE HYBRID PHOTOVOLTAICS

Erik C. Garnett, Craig Peters, Mark Brongersma, Yi Cui and Mike McGehee
Stanford Univeristy, Department of Materials Science, Stanford, CA, USA

ABSTRACT

Silicon nanowire Schottky junction solar cells have been fabricated using n-type silicon nanowire arrays and a spin-coated conductive polymer (PEDOT). The polymer Schottky junction cells show superior surface passivation and open-circuit voltages compared to standard diffused junction cells with native oxide surfaces. External quantum efficiencies up to 88% were measured for these silicon nanowire/PEDOT solar cells further demonstrating excellent surface passivation. This process avoids high temperature processes which allows for low-cost substrates to be used.

INTRODUCTION

It is now widely accepted that solar energy is a leading candidate for large-scale renewable power generation. Despite a remarkable increase in production capacity and decrease in cost over the last decade, photovoltaics are still 2-5 times more expensive than traditional power sources. One strategy for further cost reduction is to use a lower quality silicon for the starting wafer, which is a major contributing component to the overall cell cost. This approach does not work well in planar silicon solar cells because the minority carrier diffusion length becomes smaller than the thickness of silicon needed to absorb most of the above-band gap photons. To avoid this problem, there has been significant interest in recent years in using a radial p-n junction which allows for short charge separation lengths even in thick samples [1-3]. A second approach to reduce the cost of silicon solar cells is to use a much thinner high purity silicon wafer, reducing the quantity of silicon needed and thus the cost of the cell. Due to silicon's poor absorption coefficient in the red and infrared parts of the solar spectrum, planar silicon solar cells that are only a few microns thick are less than half as efficient as thick silicon cells even with traditional light trapping schemes, primarily due to a low photocurrent. However, recent work has demonstrated that periodic silicon nanowire arrays fabricated from sub-10 micron absorbers have extraordinary light trapping capabilities with optical path length enhancement factors up to 73 over the integrated AM1.5 solar spectrum [1]. Unfortunately, the high-temperature diffusion and surface passivation steps involved in standard silicon solar cell fabrication are not compatible with low-cost substrates such as glass, plastic and aluminum foil. To ameliorate this problem we have developed silicon nanowire Schottky junction solar cells that use a transparent conductive polymer (polyethylenedioxythiophene: PEDOT) instead of a metal to form the junction. As demonstrated nearly twenty years ago on planar substrates, conductive polymers with high work functions deposited on n-type silicon show open-circuit voltages (V_{oc}) approximately equal to the theoretical maximum for a given minority carrier diffusion length [4]. This is quite different from metal-semiconductor junction solar cells that almost always show much lower V_{oc} than expected from theoretical calculations due to Fermi level pinning. The lack of Fermi level pinning in the n-Si/conductive polymer system suggests surface dangling bonds are effectively passivated in this device. Since nanowire solar cells have a much larger surface area than planar cells, surface passivation is even more important.

RESULTS AND DISCUSSION

Since the previous work on planar n-Si/conductive polymer solar cells did not use PEDOT, which is the most common conductive polymer in organic solar cells and light emitting diodes, first we compared a n-Si/PEDOT solar cell to a standard diffused p-n junction cell. We started with a highly doped ($\sim1*10^{20}$ cm^{-3}) n-type wafer that has a moderately doped ($\sim1*10^{17}$) n-type

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epitaxial layer on top that is 4.5 microns thick. Due to the high doping level in the base wafer, the minority carrier diffusion length is very short (<500 nm), which means that only carriers generated in the epitaxial layer contribute significantly to the solar cell photocurrent. This scheme provides a simple method for measuring optically thin silicon solar cells without the difficulty of handling mechanically fragile samples. These epitaxial wafers were cleaned with buffered hydrofluoric acid (BHF) to remove the native silicon oxide layer and either diffused with boron to make a p-n junction or coated with PEDOT by spincoating. Evaporated silver finger grids were used as the top contact.

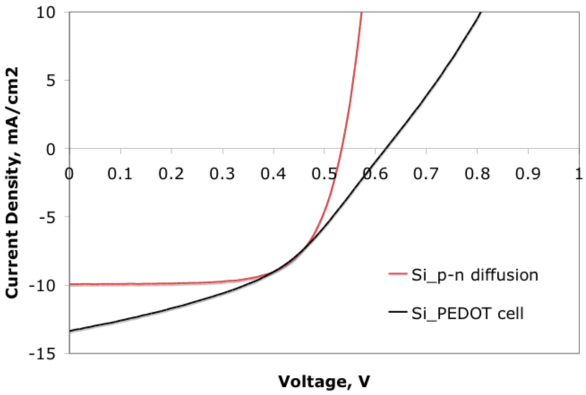

Figure 1. Planar p-n junction and n-Si/conductive polymer solar cells.

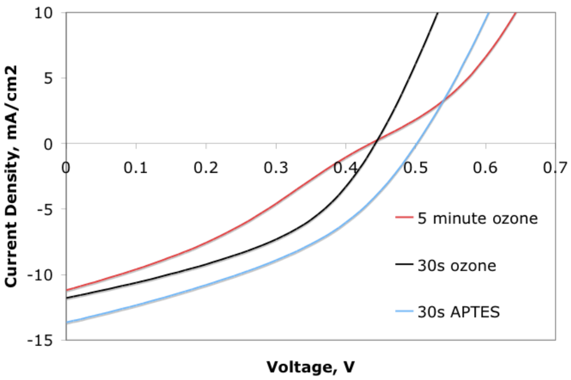

Figure 2. Output characteristics of silicon nanowire/PEDOT solar cell after various surface treatments.

Figure 1 shows the output characteristics of both cells under AM1.5G solar illumination. The n-Si/PEDOT cell shows significantly higher V_{oc} and short-circuit photocurrent density (J_{sc}) than the diffused cell but a lower fill factor (FF). The improved V_{oc} and J_{sc} both correspond to reduced surface recombination, while the lower FF stems from the significantly higher sheet resistance in the conductive polymer compared to the highly boron-doped silicon diffusion layer. Since the standard p-n junction did not have any surface passivation layer other than the native oxide that forms in air, the improved V_{oc} and J_{sc} indicate that PEDOT provides superior passivation compared to native oxide. With this proof of concept in planar solar cells, we moved on to silicon nanowire (Si NW) arrays fabricated according to a previously established procedure.[1] Figure 2 shows the output characteristics of the Si NW/PEDOT hybrid solar cells with various surface treatments.

All samples were first cleaned with BHF and then treated with UV-ozone or aminopropyl triethoxysilane (APTES) to allow for improved wetting on the rough silicon surface. The UV-ozone treatments accelerate the formation of a thin oxide layer on the silicon surface while the APTES makes the surface more hydrophilic with only minimal oxide formation. The decrease in V_{oc} and J_{sc} with the 30s ozone treatment suggests that native oxide on the surface leads to enhanced surface recombination. The reduction in FF and J_{sc} for the longer ozone treatment indicates a thicker oxide layer is forming, which leads to an increased series resistance.

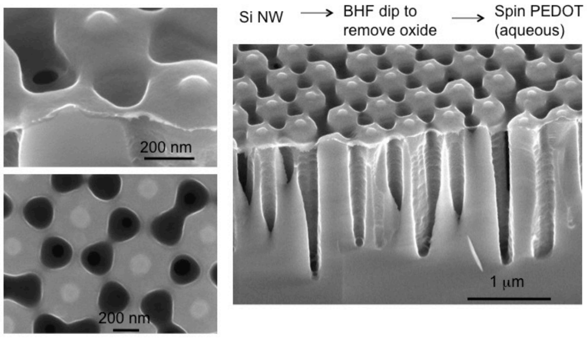

Figure 3. Tilted cross-sectional and top view SEM images of the silicon nanowire/PEDOT solar cells.

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In order to try and probe the clean Si NW/PEDOT surface directly, we added a wetting agent (0.1% by weight ZONYL-FSH, Dupont) to the PEDOT, which enables spincoating directly on the hydrogen-terminated Si NW array. Figure 3 shows tilted cross-sectional and top view scanning electron microscope (SEM) images of such a device. The polymer makes nearly a continuous film on top of the array but does not penetrate far down into the gaps between the nanowires. This filling will be improved in the future by using conductive polymer solutions with lower surface tensions. Figure 4 shows the output characteristics of Si NW/PEDOT devices with and without silver nanowires (Ag NWs) as a transparent top electrode used to reduce the top contact series resistance. The Ag NWs were synthesized by the standard polyol process [5] and deposited on the solar cells using dropcasting or a pressing method previously reported to make transparent top contacts in organic solar cells [6]. Several conclusions can be drawn from this data: the PEDOT/Si NW devices that use a wetting agent instead of surface functionalized APTES perform better due to lower surface recombination, Ag NW transparent top electrodes increase the J_{sc} and FF by lowering the top contact series resistance (they are much more conductive than the PEDOT), but they also lower the V_{oc} because of increased shunting in small gaps in the polymer where direct Ag/Si contact is possible. Although Ag should form a Schottky barrier on n-type silicon, metals often have lower than expected barrier heights due to Fermi level pinning as mentioned earlier.

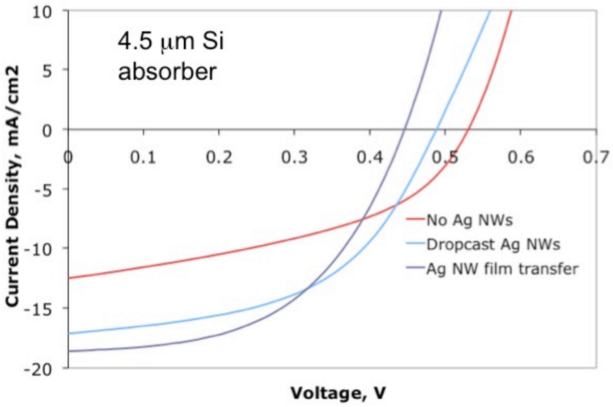

Figure 4. Output characteristics of silicon nanowire/PEDOT solar cells after BHF only.

We also performed laser beam induced current (LBIC) on our Si NW/PEDOT devices. LBIC uses a focused laser beam and a scanning stage to map out the photocurrent distribution over a sample. It is an invaluable tool used to identify defective regions and determine device uniformity in photovoltaics. Figure 5 shows an LBIC map of a Si NW/PEDOT solar cell that has a 100 nm thick silver electrode finger without a Ag NW transparent top contact. From the LBIC map it is clear that the photocurrent drops off significantly when moving more than about 1 mm away from the metal electrode due to poor electrical transport in the PEDOT layer. However, outside of this effect the current is fairly uniform, at least at the micron-scale resolution available with LBIC. The map also demonstrates that by measuring the solar cell current within 1 mm of the silver finger electrode we can see the intrinsic performance without significant contributions from the PEDOT sheet resistance.

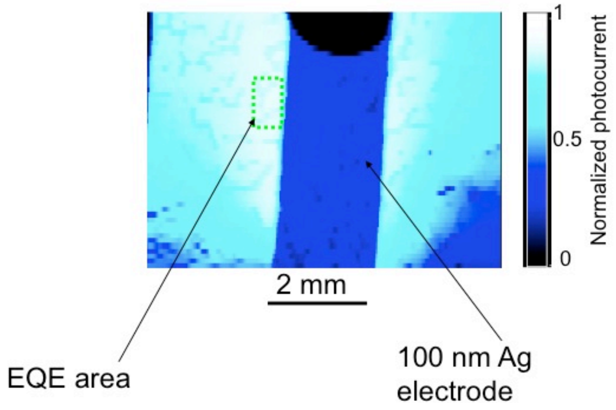

Figure 5. Laser beam induced current map of silicon nanowire/PEDOT solar cell.

Finally, we performed external quantum efficiency (EQE) measurements on the Si NW/PEDOT hybrid solar cells, shown in Figure 6. The EQE was measured in an area within 1 mm of the silver electrode finger as shown in figure 5. The maximum EQE was 88%

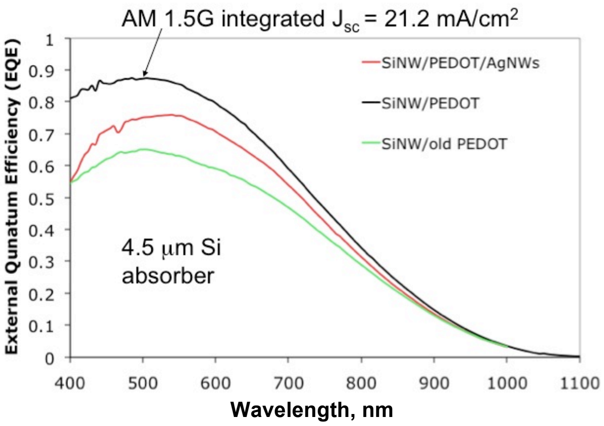

Figure 6. External quantum efficiency of silicon nanowire/PEDOT solar cells.

and above 80% over most of the visible region. Since the nanowire arrays typically show about 10-20% reflection over the visible part of the solar spectrum [7], the internal quantum efficiency (IQE) must be nearly 100% in that wavelength range, again indicating excellent surface passivation by the PEDOT. The EQE in the red and IR range is lower for two reasons. First, these nanowire arrays are only 2 microns long and therefore should only have minimal light trapping effects according to previous measurements [1]. Second, silicon's absorption coefficient is smaller at longer wavelengths, which means that the red and IR photons are absorbed further down into the nanowire array where the polymer is not effectively penetrating and passivating the surface. This should lead to a lower IQE for longer wavelengths. Further studies to confirm this are in progress. Integrating the EQE over the solar spectrum gives a J_{sc} of 21.2 mA/cm^2. Using this value for J_{sc} along with the measured V_{oc} and FF from the output characteristics gives a small area conversion efficiency of 6.1% for a 4.5 micron thin device.

CONCLUSIONS

Schottky solar cells made using n-type silicon and a conductive polymer (PEDOT) showed improved performance over standard diffused junction solar cells due to improved surface passivation. The polymer Schottky junction approach was effective for both planar and nanowire array solar cells and therefore offers a simple, fast and inexpensive method for making silicon nanowire solar cells on low-cost substrates that are not compatible with standard high temperature processes such as post-implantation annealing, diffusion and thermal oxidation. The polymer serves both to form the junction and passivate the surface, simplifying the fabrication procedure. External quantum efficiencies up to 88% on the Si NW/PEDOT solar cells demonstrate the high quality of this process, which considering reflection losses, leads to internal quantum efficiencies near 100%. Further improvements in light trapping, polymer coating, and top contact sheet resistance should lead to efficiencies above 10% for thin silicon nanowire solar cells on low-cost substrates.

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REFERENCES

[1] Garnett, E. and Yang, P., "Light Trapping in Silicon Nanowire Solar Cells" *Nano Letters*, **10**, 2010, pp. 1082-1087.

[2] Garnett, E.C. and Yang, P**.,** "Silicon Nanowire Radial p-n Junction Solar Cells" *J. Am. Chem. Soc.* **130**, 2008, pp. 9224-9225.

[3] Kayes, B. et al., "Comparison of the device physics principles of planar
and radial p-n junction nanorod solar cells" *J. Appl. Phys.* **97**, 2005, pp. 114302.

[4] Sailor, M.J. et al. "Thin Films of n-Si/Poly-$(CH_3)_3$Si-Cyclooctatetraene: Conducting-Polymer Solar Cells and Layered Structures" *Science* **249**, 1990, pp. 1146-1149.

[5] Sun, Y. et al., “Crystalline Silver Nanowires by Soft Solution Processing” *Nano Letters* **2**, 2002, pp. 165-168.

[6] Gaynor, W. et al. “Fully Solution-Processed Inverted Polymer Solar Cells with Laminated Nanowrie Electrodes” *ACS Nano* **4** 2010, pp. 30-34.

[7] Zhu, J. et al. “Optical Absorption Enhancement in Amorphous Silicon Nanowire and Nanocone Arrays” *Nano Letters* **9**, 2009, pp. 279-282.