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Final Report

Semiconducting Nanowire Solar Cells for Enhanced Energy Harvesting

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Background

Solar cells are attractive candidates for generating clean and renewable energy. Nanowires (NWs) due to their unique electrical and optical properties offer new opportunities to solar cells for reduced cost and improved efficiency. Although SiNWs have been already demonstrated as promising solar cell elements[1], to harness the full potential of SiNWs, SiNW solar cells require further characterizations and optimizations, including device integrations of SiNWs and surface treatments of SiNWs. Herein we report three main research results to characterize and optimize the performance of SiNW solar cells: 1) single and tandem axial p-i-n SiNW solar cells, 2) direct growth of SiNW solar cells, and 3) effective junction and surface passivation strategies for Si wire radial junction solar cells.

Single and Tandem Axial p-i-n SiNW Solar Cells

Semiconducting NWs synthesized by bottom-up approaches are promising building blocks for solar cells, because the composition, size, and morphology of NWs can be precisely controlled at the nanoscale[2]. We have first experimentally realized that axially dopant modulated p-i-n SiNW (Figure 1a) and tandem p-i-n+-p+-i-n SiNW (Figure 1b) can serve as a solar cell element. The SiNWs were grown by using vapor-liquid-solid mechanism[3], and the dopant modulation within a single SiNW was achieved by changing precursor gases during the growth. Next, the SiNWs sonicated off from the growth substrate were transferred to the device substrate, and the electrical connection was made by using electron beam lithography. Figure 1c illustrates the representative I-V curves of the SiNWs. A single axially dopant modulated p-i-n SiNW exhibits 0.5% of solar power conversion efficiency (0.29V of V_{oc}, 3.5 mA/cm^2 of J_{sc}, and 0.51 of FF) under simulated one sun solar conditions (AM1.5G), and the tandem SiNW performs 1.57 times higher V_{oc} than the p-i-n SiNW. This result holds significant promise for the further development of nanoscale solar energy conversion system.

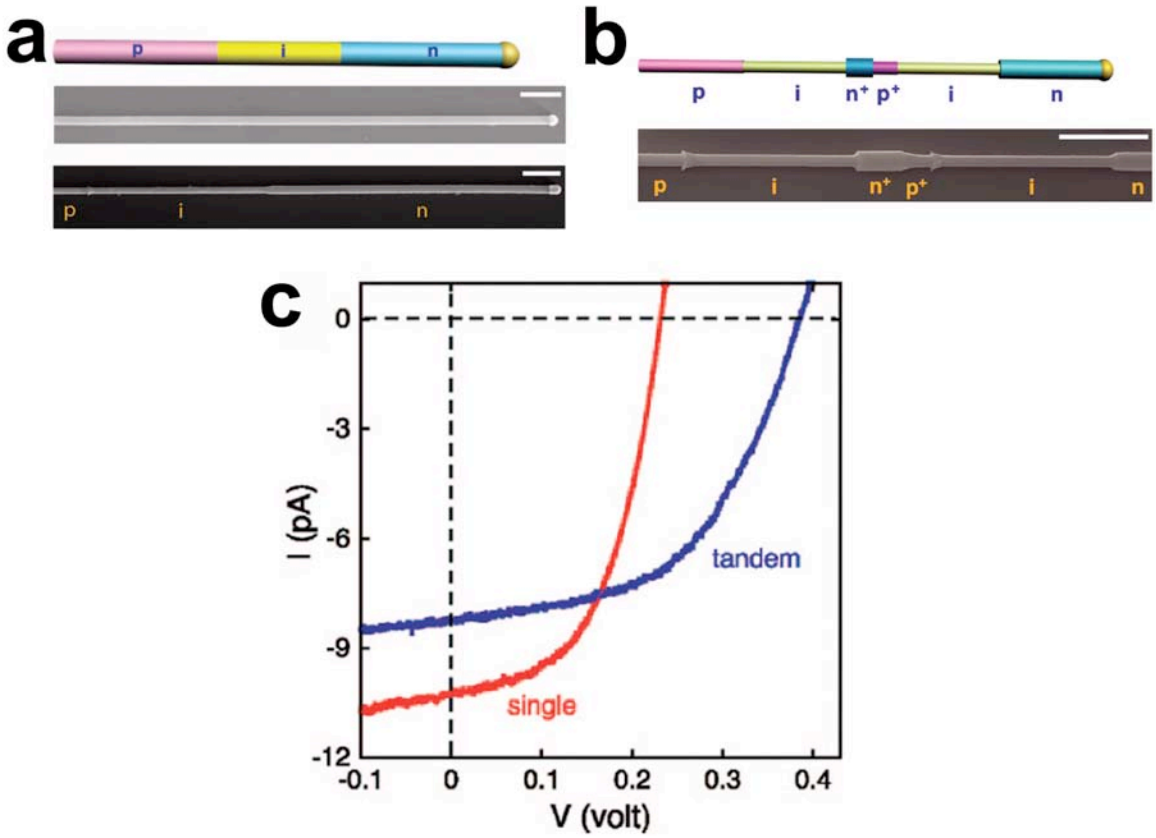
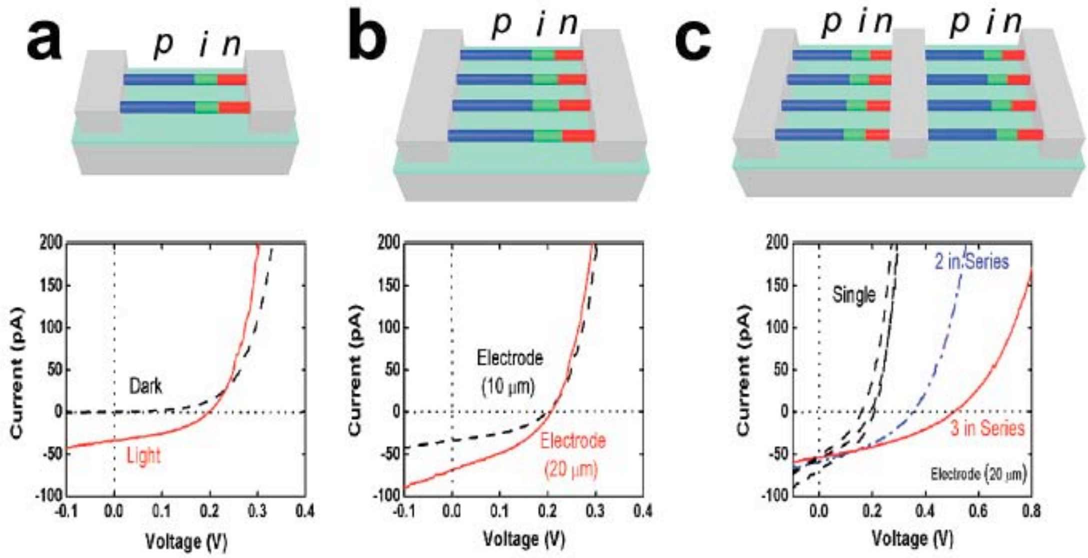


Figure 1. **a)** Schematic and SEM images of a single p-i-n SiNW. The bottom SEM image shows a single p-i-n SiNW after selective wet etching. Heavily doped n-type region is slowly etched, compared to the p- and i-type Si regions. **b)** Schematic and SEM images of a tandem p-i-n+-p+-i-n SiNW. **c)** Representative I-V curves of a single p-i-n SiNW and a tandem SiNW. Scale bars are 1 μm.

Direct Growth of SiNW Solar Cells

One of the unique advantages of semiconducting NWs is the capability to tune up the composition of NWs at the nanoscale during the growth, and the composition modulated NWs, for example, axially dopant modulated p-i-n SiNWs, can serve as promising solar cell elements. However, in order to make full use of the potential of semiconducting NWs, the integration of semiconducting NWs into functional devices has to be further developed with high controllability, repeatability, and scalability. Therefore, we have experimentally demonstrated a novel and simple method to directly grow NW-based functional devices, named as Direct Growth of Nanowire Devices (DGND), consisting of both homogeneous and axially modulated heterogeneous NWs with controlled alignment and orientation of NWs, and designed spacing and electrical connections. Our DGND method is based on the epitaxial growth of SiNWs from the sidewalls of heavily doped Si electrodes and on the matching of the electrode patterns with the synthesis conditions to electrically connect SiNWs during the NW synthesis step. Because SiNWs can be epitaxially and directionally grown from one sidewall of Si electrodes, the orientation of axially dopant modulated p-i-n SiNWs can be easily controlled by using our method.

With the DGND method, we have successfully grown several NW-based devices, including resistors, diodes, diode logic gates, and scalable solar cell elements with high uniformity, reproducibility, and comparable performance to the previously reported NW devices. In particular, we have demonstrated that our directly grown, axially dopant modulated p-i-n SiNWs can be readily extended in series and in parallel to produce scalable maximum power (Figure 2), which can be enough to drive NW- or nanotube (NT)-based electronic devices. More importantly, our method can be further extended to grow NW devices with various materials, such as Ge, SiGe, GaAs, GaP, InAs, and InP.



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		a	b	c (2 in series)	c (3 in series)
Electrode Width		**10 μm**	**20 μm**	**20 μm**	**20 μm**
I_{sc}	(pA)	33.4	68.5	58.5	53.6
V_{oc}	(V)	0.196	0.208	0.352	0.508
FF	(-)	0.418	0.395	0.368	0.356
P_{max}	(pW)	2.7	5.6	7.6	9.7

Figure 2. Direct growth of SiNW solar cells in parallel and in series. **a)** (Top) Schematic and (Bottom) dark (dashed line) and light (solid line) I-V curves of the as-grown p-i-n SiNW solar cells. **b)** (Top) Schematic and (Bottom) light I-V curves of the SiNW solar cells with 10 μm wide and 20 μm wide electrodes respectively. Both I_{sc} and P_{max} were doubled by increasing the electrode width, which is equivalent to assembling two solar cell elements in parallel. **c)** (Top) Schematic and (Bottom) light I-V curves of the SiNW solar cell elements in single, double, and triple serial connections. The V_{oc} scaled with the number of series-connected solar cell elements. All electrodes are 20 μm wide. **d)** Summary table of the photovoltaic properties of SiNW solar cell elements in Figure 2a-2c.

Effective Junction and Surface Passivation Strategies for Si Wire Radial Junction Solar Cells

Si wire-based radial junction solar cells were proposed to have a theoretical efficiency of 17% due to improved charge-carrier collection[4], but reported experimental efficiencies are typically below 10%. It is well recognized that such wire-based radial junction wire solar cells inherently suffer from large junction and surface charge-carrier recombination, but this has received limited experimental investigation. Therefore, we have developed two strategies for effective junction and top surface passivation for wire-based radial junction solar cells by using intrinsic polycrystalline Si (poly-Si) and amorphous silicon nitride (a-SiN:H) thin films, respectively. As shown in Figure 3a, we fabricated the vertically-aligned radial junction wire arrays from a bulk Si wafer to form a hybrid Si microwire (radial junction) and planar solar cells to simplify the fabrication process so that we can focus on the passivation methods. The inclusion of the intrinsic poly-Si layer between the p-n junction layers increases the efficiency by approximately 30% by reducing the dark current. The top a-SiN:H layer improves the efficiency by approximately 20% due to its combined surface passivation and anti-reflection effects. With the combination of both passivation layers, the maximum efficiency of the hybrid Si microwire-planar cell is improved from 7.2% to 11.0% under AM 1.5G illumination (Figure 3b). The efficiency of the hybrid cells is also higher than that of planar cells of the identical layers, confirming the benefits of radial junction in terms of enhancing light absorption and improving the charge-carrier collections. More importantly, these junction and surface passivation strategies are effective to other wire-based radial-junction solar cells as well. Finally, the hybrid cell structure serves as an important intermediate between planar and pure wire array-based solar cells in that it has higher efficiency than planar comparison solar cells and simpler fabrication than pure wire array-based solar cells.

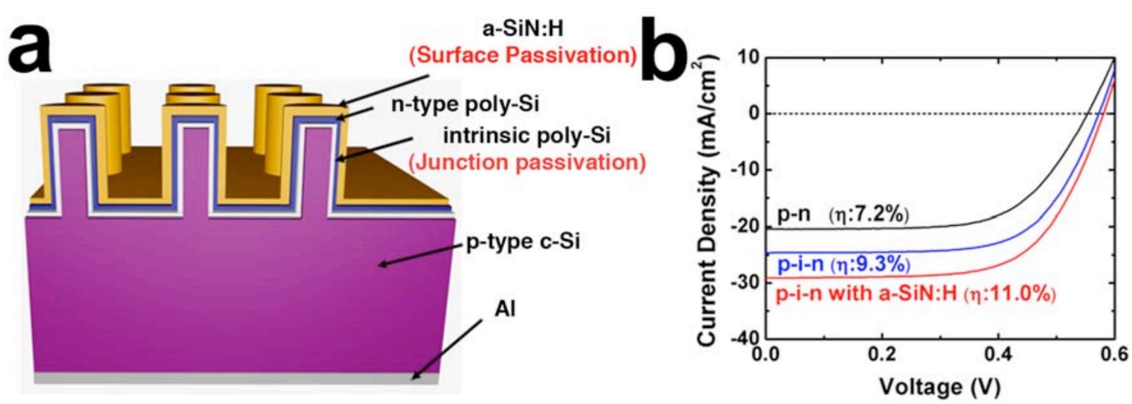

Figure 3. **a)** Schematic of a vertically aligned hybrid Si microwire (radial junction) and planar solar cell. **b)** Representative I-V curves of the hybrid solar cells, showing effective junction and surface passivations.

Conclusion

We have first experimentally demonstrated that single and tandem axially dopant modulated p-i-n SiNWs can serve as a promising building block for nanoscale solar energy conversion system. In addition, we have developed a novel and simple method to directly grow NW-based functional devices, which can readily integrate axially dopant modulated p-i-n SiNWs into solar cells both in parallel and in series. The maximum power of SiNW solar cells, realized by using our methods, is scalable to drive NW- or NT-based electronic devices, thereby potentially enabling self-powered nanoscale functional devices. Furthermore, we have investigated the effective junction and surface passivation strategies for vertically aligned Si wire radial junction solar cells which suffer from deteriorate junction and surface recombinations due to their inherent large surface areas. As a result, the maximum efficiency of our hybrid Si microwire-planar solar cells increases from 7.2% to 11.0% by using our proposed passivation strategies for both the p-n junction and the top surface by the intrinsic poly-Si layer and the a-SiN:H layer, respectively. As such, further characterizations and optimizations of semiconducting NW solar cells can lead to significant, appreciable opportunities for solar cells with competitive efficiency and demonstrable cost benefits.

Reference

1. Tian, B. Z.; Zheng, X. L.; Kempa, T. J.; Fang, Y.; Yu, N.; Yu, G.; Huang, J.; Lieber, C. M. *Nature* **2007**, 449, 885-888.
2. Cui, Y.; Lauhon, L. J.; Gudiksen, M. S.; Wang, J.; Lieber, C. M. *App. Phys. Lett.* **2001**, 78, 2214-2216.
3. Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, 4, 89-90.
4. Kelzenberg, M. D.; Boettcher, S. W.; Petykiewicz, J. A.; Turner-Evans, D. B.; Putnam, M. C.; Warren, E. L.; Spurgeon, J. M.; Briggs, R. M.; Lewis, N. S.; Atwater, H. A. *Nature Mater.* **2010**, 9, 239-244.

Journal Publications

Journals listed below were published during the financial support by Link Energy Fellowship, which was acknowledged in all the paper.

1. Chi Hwan Lee, **Dong Rip Kim**, Xiaolin Zheng, "Fabrication of Nanowire Electronics on Non-conventional Substrates by Water-Assisted Transfer Printing Method," *Nano Letters*, 11 (2011), 3435-3439.
   - **Highlighted by Stanford News, Materials Today, and EE Times, July 2011.**
2. **Dong Rip Kim**, Chi Hwan Lee, Pratap Mahesh Rao, In Sun Cho, Xiaolin Zheng, "Hybrid Si Microwire and Planar Solar Cells: Passivation and Characterization," *Nano Letters*, 11 (2011), 2704-2708.
3. Jeffery Michael Weisse, **Dong Rip Kim**, Chi Hwan Lee, Xiaolin Zheng, "Vertical Transfer of Uniform Silicon Nanowire Arrays via Crack Formation," *Nano Letters*, 11 (2011), 1300-1305.
4. Chi Hwan Lee, **Dong Rip Kim**, Xiaolin Zheng, "Orientation-Controlled Alignment of Axially Modulated pn Silicon Nanowires," *Nano Letters* 10 (2010), 5116-5122.
5. Yunzhe Feng, Pratap Mahesh Rao, **Dong Rip Kim**, Xiaolin Zheng, "Methane Oxidation Over Catalytic Copper Oxides Nanowires," *Proc. Combust. Inst.* 33 (2011), 3169-3175.
6. Chi Hwan Lee, **Dong Rip Kim**, Xiaolin Zheng, "Fabricating nanowire devices on diverse substrates by simple transfer-printing methods," *Proc. Natl. Acad. Sci.* U.S.A. 107 (2010), 9950-9955.
7. **Dong Rip Kim**, Chi Hwan Lee, Xiaolin Zheng, "Direct Growth of Nanowire Logic Gates and Photovoltaics," *Nano Letters* 10 (2010), 1050-1054.
8. **Dong Rip Kim**, Chi Hwan Lee, Xiaolin Zheng, "Probing Flow Velocity with Silicon Nanowire Sensors," *Nano Letters* 9 (2009), 1984-1988.
9. **Dong Rip Kim**, Xiaolin Zheng, "Numerical Characterization and Optimization of the Microfluidics for Nanowire Biosensors," *Nano Letters* 8 (2008), 3233-3237.
10. Thomas J. Kempa, Bozhi Tian, **Dong Rip Kim**, Jinsong Hu, Xiaolin Zheng, and Charles M. Lieber, "Single and Tandem Axial p-i-n Nanowire Photovoltaic Devices," *Nano Letters* 8 (2008), 3456-3460.
    - **Cited by 100+ publications.**