

PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://spiedigitallibrary.org/conference-proceedings-of-spie)

Nanostructures for high-efficiency photovoltaics

Harry A. Atwater

Harry A. Atwater, "Nanostructures for high-efficiency photovoltaics," Proc. SPIE 7047, Nanoscale Photonic and Cell Technologies for Photovoltaics, 704702 (11 September 2008); doi: 10.1117/12.801575

SPIE.

Event: Solar Energy + Applications, 2008, San Diego, California, United States

Nanostructures for High Efficiency Photovoltaics

Harry A. Atwater

Thomas J. Watson Laboratory of Applied Physics

California Institute of Technology

Pasadena CA, 91125

ABSTRACT

Photovoltaics (PV) technology is currently enjoying substantial growth and investment, owing to worldwide sensitivity to energy security and the importance of renewable energy as a means to mitigate carbon emissions. There are many options in photovoltaic cell design and fabrication, but the key performance metric is the cost per Watt of PV-generated electricity. While solar cells are semiconductor devices like integrated circuits, the processing cost/area must be several orders of magnitude less expensive than for microelectronic integrated circuit chip processing. Thus while most current solar cell manufacturing is done with crystalline silicon wafers, the future of photovoltaics could see the large-scale development of inexpensive thin film and nano-structured devices and processes. To achieve substantial market growth to the point where photovoltaics is able to seriously contribute to the overall energy supply, high solar conversion efficiency will be critical, as will be the use of earth-abundant materials in thin film cells. This paper surveys several promising new approaches to ultrahigh efficiency thin film multi-junction solar cells, options for earth-abundant materials, semiconductor nanowire-based solar cells and plasmonic structures for enhanced light absorption that open up new design approaches to very thin photovoltaic devices.

Keywords: nanostructure, photovoltaic, solar cell, plasmon, nanowire, multijunction, earth-abundant materials

1. PLASMONIC PHOTOVOLTAICS

Metallic nanostructures can excite surface plasmons and can dramatically increase the optical path length in thin active photovoltaic layers to enhance overall photoabsorption [1-5]. This effect has potential for cost and weight reduction with thinned layers and also for efficiency enhancement associated with increased carrier excitation level in the absorber layer. We have observed short-circuit current and efficiency enhancements under AM1.5G solar spectrum for GaAs cells with dense arrays of Ag nanoparticles deposited through porous alumina membrane masks, relative to reference GaAs cells with no metal nanoparticle array[6]. This photocurrent enhancement is attributed to the scattering effects of metal nanoparticles for light incident into photovoltaic layers. A simple optical model representing metal nanoparticle surface plasmon resonances and multi-angle scattering has been developed and well explains the spectral behavior of the experimental photocurrent enhancement [7]. A novel ultrathin GaAs cell structure with a metallic back layer has been also developed with a bonding and layer transfer technique. This waveguide-like GaAs cell showed significant enhancements in short-circuit current density and efficiency relative to reference GaAs cells with an absorbing GaAs back layer due to a Fabry-Perot resonance in the air/semiconductor/metal heterostructure.

2. SILICON WIRE ARRAY PHOTOVOLTAICS

Silicon wire array cells based on use of radial pn junctions are of interest in photovoltaics because of their potential to reduce the materials costs associated with cell fabrication. However, devices fabricated to date based on Au-catalyzed vapor-liquid-solid growth have suffered from low open-circuit voltages (to our knowledge the highest reports are 260 mV in the solid state and 389 mV in solid-liquid junctions). Herein we report on the potential of low-cost catalysts such as Cu and Ni to fabricate Si wire arrays with potentially higher minority-carrier lifetimes than is possible with a Au catalyst, as well as on the use of reactive ion etching to fabricate high-purity analogs to vapor-liquid-solid grown arrays.

We have previously reported on the potential of radial pn junction wire array solar cells, that is, cells which consist of a dense array of semiconducting wires where each wire has a pn junction in the radial direction (Fig. 1), to reduce the materials costs associated with photovoltaic (PV) device fabrication [8,9]. Recently, PV devices based on Si nanowires with radial pn junctions have been demonstrated experimentally, both at the single-wire [10], and at the large-area [11] level. Also, semiconductor-liquid junctions based on large-area wire arrays have been reported [12,13]. In all

cases, the wires were grown by the vaporliquid-solid (VLS) process [14], using Au as the catalyst. While these results are impressive, the open-circuit voltages (V_{oc} s) reported in each case (up to 260 mV, 130 mV, 389 mV, and 230 mV respectively) are relatively low for Si devices, possibly implying a trap density near the junction that is too high to allow for high-quality devices. It would therefore be desirable to explore the geometrical effects on photovoltage of the radial pn junction geometry independent of the effects of catalyst incorporation, as well as to explore the fabrication of wire arrays with catalysts less injurious to the properties of Si than Au is. Here we report on the fabrication of large area wire arrays using Ni and Cu catalysts that may be less detrimental to the PV properties of Si than Au is. We also report on the solid state characterization of reactive ion etched (RIE) wire arrays that serve as a model analog to grown wire arrays, and provide insight into the effects of morphology on device performance without convolution with the effects of catalyst incorporation.

3. MULTIJUNCTION SOLAR CELLS

Multijunction solar cells hold the photovoltaic conversion efficiency records for 1 Sun and concentrated conversion efficiency. To simultaneously achieve dislocation-free material and an optimal bandgap sequence for conversion of the solar spectrum in four or more junction solar cells, lattice-mismatched structures will be required. While current metamorphic growth techniques are proving useful in three junction cell applications[15-18], they are limited in the degree of mismatch that they can accommodate. Wafer bonding, on the other hand, can accommodate any degree of lattice mismatch and isolate the defects at the bonded interface between mismatched layers. In this way, materials with a wide variety of lattice parameters can be integrated into a single device.

In our approach to development of a near optimal four-junction solar cell, we use templates for subcell growth employing two lattice parameters, and two bonded interfaces. The first brings together our active material systems, which are based on the GaAs and InP lattice constants. The second allows us to utilize a Si substrate as the overall cell substrate rather than an expensive InP substrate. The final structure will consist of a GaInP/GaAs/GaInAsP/GaInAs four junction solar cell on a Si substrate. Toward this end, we have developed a process for fabrication and characterization of GaInP/GaAs dual junction solar cells on Ge/Si epitaxial templates. In other work, we have demonstrated other including high quality InGaAs solar cells on InP/Si templates[19] as well as low-resistance bonded interfaces between GaAs and InP wafers[20].

4. EARTH ABUNDANT SEMICONDUCTOR FOR PHOTOVOLTAICS

As photovoltaics scales to a manufacturing capacity beyond 50 GW/yr, consideration of the total abundance of photovoltaic materials in the earth's crust, as well as the economically recoverable materials resource, will place constraints on the materials that are useful for photovoltaic modules and systems. Some of the materials in use in photovoltaics today, such as CuInGaSe₂ and CdTe thin film absorbers and Ag metallization, may not be sufficiently abundant for use in solar power systems at very large scale. Thus it is important to identify "earth abundant" semiconductor materials which are suitable photovoltaic device quality materials whose elemental constituents are abundant with large resource bases.

As an example, we consider the compound semiconductor Zn₃P₂. Semiconducting Zn₃P₂ is an earth-abundant material that has shown promise for solar energy conversion but has not been investigated as thoroughly as other thin film materials. It exhibits a direct energy gap near the terrestrial optimum (1.5 eV) [21] and is composed of earth abundant constituent elements. Predominantly p-type doping has been observed in Zn₃P₂, requiring photovoltaic devices to use Schottky barriers and semiconductor heterojunctions. The record solar energy conversion efficiency for a device with a Zn₃P₂ absorber was set in 1979, reaching 6.08% with a diffused Mg₃P₂ heterojunction [22]. Despite considerable effort, other device structures using p-n heterojunctions have not demonstrated good performance [23].

We have synthesized Zn₃P₂ bulk single crystal samples and have investigated surface passivation and Schottky barrier formation[24]. Open circuit voltage in Zn₃P₂ cells has been limited by Fermi-level pinning due to surface states and heterojunction interdiffusion, motivating the need to prepare interfaces that are electrically passive and chemically inert. We investigated the surface chemistry of Zn₃P₂ etched with bromine in methanol and passivated with ammonium sulfide in t-butanol. The treatment decreases surface oxidation as determined by X-ray photoelectron spectroscopy and provides a stable, low-defect interface as monitored by steady-state photoluminescence. Magnesium Schottky diodes fabricated with sulfur-passivated interfaces show evidence of enhanced barrier heights in comparison to control devices.

REFERENCES

- [1] Stuart, H. R. and Hall D. G., *Appl. Phys. Lett.* 69, pp. 2327-2329 (1996)
- [2] Stuart, H. R. and Hall D. G., *Appl. Phys. Lett.* 73, pp. 3815-3817 (1998)
- [3] Schaadt, D. M., et al, *Appl. Phys. Lett.* 86, pp. 063106-1-063106-3 (2005)
- [4] S. Pillai et al, *Appl. Phys. Lett.* 88, pp. 161102-1-161102-3 (2006)
- [5] S. Pillai et al, *J. Appl. Phys.* 101, pp. 093105-1-161102-8 (2007).
- [6] Tanabe, K, Nakayama K and Atwater, HA, "Plasmon-Enhanced Absorption and Photocurrent In Ultrathin GaAs Solar Cells with Metallic Nanostructures", *Proc. of 33rd IEEE Photovoltaics Specialists Conference*, pp (2008).
- [7] Bohren, C. F. and Huffman, D. R. *Absorption and Scattering of Light by Small Particles* (Wiley, New York), Chap. 3 -5 (1983). Davis, A., R., Bush, C., Harvey, J. C. and Foley, M. F. , "Fresnel lenses in rear projection displays," *SID Int. Symp. Digest Tech. Papers* 32(1), 934-937 (2001).
- [8] Kayes, B.M. et al., "Radial PN Junction Nanorod Solar Cells: Device Physics Principles and Routes to Fabrication in Silicon", *Proceedings of 31st IEEE Photovoltaics Specialist Conference*, pp. 55-58 (2005)
- [9] Kayes, B.M. , Atwater, H. A. and Lewis, N. S. "Comparison of the Device Physics Properties of Planar and Radial pn Junction Nanorod Solar Cells", *J. Appl. Phys.* 97, Art. No. 114302 (2005).
- [10] Tian, B.Z. et al., "Coaxial Silicon Nanowires as Solar Cells and Nanoelectronic Power Sources", *Nature* 449, pp. 885-890, (2007).
- [11] Tsakalakos, L. et al., "Silicon Nanowire Solar Cells", *Appl. Phys. Lett.* 91, Art. No. 233117, (2007).
- [12] Maiolo, J.R. et al., "High Aspect Ratio Silicon Wire Array Photoelectrochemical Cells", *J. Amer. Chem. Soc.* 129, , pp. 12346-12347, (2007).
- [13] Goodey, A.P. et al., "Silicon Nanowire Array Photoelectrochemical Cells", *J. Am. Chem. Soc.* 129, pp. 12344 - 12345, (2007)
- [14] Wagner, R.S. and Ellis, W.C. "Vapor-Liquid-Solid Mechanism of Single Crystal Growth", *Appl. Phys. Lett.* 4, , pp. 89-90, (1964).
- [15] King, R.R., Law, D.C., Edmondson, K.M., Fetzer, C.M., Kinsey, G.S., Yoon, H., Sherif, R. and Karam, N.H. "40% efficient metamorphic GaInP/GaInAs/Ge multijunction solar cells," *Applied Physics Letters*, vol. 90, Apr 2007.
- [16] C. M. Fetzer, H. Yoon, R. R. King, D. C. Law, T. D. Isshiki, and N. H. Karam, "1.6/1.1 eV metamorphic GaInP/GaInAs solar cells grown by MOVPE on Ge," *Journal of Crystal Growth*, vol. 276, pp. 48-56, Mar 2005.
- [17] M. Wanlass, P. Ahrenkiel, D. Albin, J. Carapella, A. Duda, K. Emery, D. Friedman, J. Geisz, K. Jones, A. Kibbler, J. Kiehl, S. Kurtz, W. McMahon, T. Moriarty, J. Olson, A. Ptak, M. Romero, and S. Ward, "Monolithic, Ultra-Thin GaInP/GaAs/GaInAs Tandem Solar Cells," in 4th World Conference on Photovoltaic Energy Conversion, Waikoloa, Hawaii, 2006, pp. 729-732.
- [18] F. Dimroth, U. Schubert, and A. W. Bett, "25.5% efficient Ga_{0.35}In_{0.65}P/Ga_{0.83}In_{0.17} as tandem solar cells grown on GaAs substrates," *IEEE Electron Device Letters*, vol. 21, pp. 209-211, May 2000.
- [19] J. M. Zahler, K. Tanabe, C. Ladous, T. Pinnington, F. D. Newman, and H. A. Atwater, "High efficiency InGaAs solar cells on Si by InP layer transfer," *Applied Physics Letters*, vol. 91, Jul 2007.
- [20] K. Nakayama, K. Tanabe, and H. A. Atwater, "Improved Electrical Properties of Wafer Bonded p-GaAs/n-InP Interfaces with Sulfide Passivation," *Journal of Applied Physics*, (in print), 2007.
- [21] E.A. Fagen, "Optical-Properties of Zn₃P₂", *J. Appl. Phys.* 50, 1979, pp. 6505-6515.
- [22] M. Bhushan, A. Catalano, "Polycrystalline Zn₃P₂ Schottky-Barrier Solar-Cells", *Appl. Phys. Lett.* 38, 1, 1981, pp. 39-41.
- [23] M. Ginting, J.D. Leslie, "Preparation and Electrical-Properties of Heterojunctions of ZnO on Zn₃P₂ and CdTe", *Can. J. Phys.* 67, 4, 1989, pp. 448-455.
- [24] Gregory M. Kimball, Nathan S. Lewis, Harry A. Atwater, *Proc. 33rd IEEE Photovoltaic Specialists Conference*, San Diego, CA, (2008).