

# Photovoltaics

# Making Every Photon Count

Researchers are turning to nanoscale structures to create more cost-effective solar cells.

ecades of research have been devoted to improving the electrical properties of photovoltaic materials. Today, some of the most notable research is in organic and hybrid materials—especially silicon. "Silicon cells have been studied for a long time from a materials science point of view, says

When the scale

smaller than

stop working.

of light-directing

1 µm, geometric

optical approaches

features becomes

Thomas F. Krauss at the University of St. Andrews in the United Kingdom. "But it's no longer sufficient to improve the material."

Krauss is the general chair of OSA's Optical Nanostructures and Advanced Materials for Photovoltaics meeting, which will be held 11-14 November in Eindhoven, the Netherlands. He explains, "We need to think about the photon flux: How do photons

get into the cell, and how do we manage them? Photovoltaics research is turning from a materials problem into a photonics problem."

Economic pressure has influenced the latest research on photon management. Over the past 30 years, the cost of solar modules has fallen by an order of magnitude, due to economies of scale, better fabrication methods and higher cell efficiency. But solar is still more expensive than many other forms of energy.

> A vast majority of the photovoltaic cells made today are comprised of silicon. They are hundreds of micrometers thick and equipped with relatively simple geometrical optics to direct light into the cell. A commonly cited number suggests that at least 40 percent of the cost of each module is for the materials. Some of the proposed

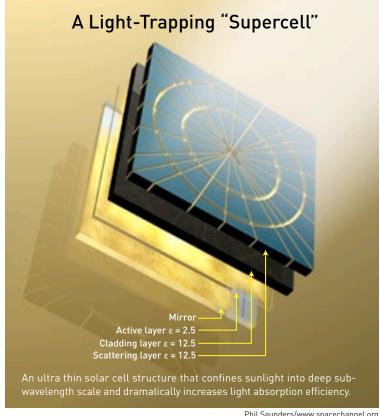
strategies for price reduction include moving to cheaper inorganic materials or even more inexpensive (but less efficient) organic ones. Here, we examine a third strategy: Stick with silicon, but use less of it.

#### Thin-film silicon cells

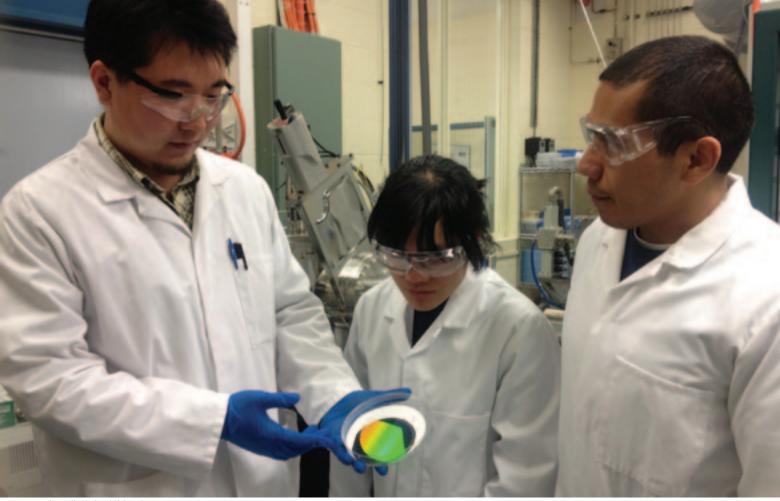
Traditionally, engineers create silicon photovoltaic cells by slicing crystalline silicon into a slab hundreds of micrometers thick. Why not just deposit a film that is only 2-um thick? Because silicon does not absorb light well, especially at red and near-IR wavelengths. To achieve reasonable absorption, thin-film silicon cells must efficiently manage light.

The light-trapping techniques used in thick cells can't be used in thin-film cells. Thick silicon cells use textured surfaces with few-micrometer-thick features that can be modeled using geometrical optics. These are effective at scattering light into the cell at angles that allow less light to escape. But for films thinner than 2 µm, there simply isn't room for that strategy.

When the scale of light-directing features becomes smaller than 1 µm, geometric optical approaches stop working. Nanophotonics processes dominate in cells whose



Phil Saunders/www.spacechannel.org



Australia National University

size is on the same scale as the wavelengths they absorb. Techniques for handling light at this scale have been developed for communications work, and some of these can be repurposed for photovoltaics.

The scope of work on using nanostructures for thin-film silicon photovoltaics is broad. Kylie Catchpole from the Australia National University and her colleagues published a review article in 2011 on recent achievements in the field. One of the interesting advances is the use of plasmonics and nanoshells to manipulate light on the nanoscale.

#### Absorption in thin films

Engineers can use nanoscale light trapping to create designs that enhance absorption beyond the limits achievable with geometrical optics. Thinner films also have the potential to improve electronic efficiency. Shanhui Fan of Stanford University, U.S.A., says, "In many photovoltaic materials, there is an intrinsic length scale mismatch between the optics and the electronics." The absorption length of light far exceeds the distance that the carriers are allowed to travel. Making thinner cells helps to

overcome such a mismatch and can potentially increase efficiency.

Fan's Stanford colleague, Yi Cui, adds, "In the past, we developed nanocone, nanowell, nanocavity and hollow nanoshell structures, trying to realize multiple functions all at once: antireflection, light trapping and enhancing charge carrier collection." Cui's group worked with other collaborators to develop high-performance and low-cost metal nanowire networks that acted as novel transparent conducting electrodes.

#### **Plasmonics**

The usefulness of plasmonics for solar cells is debatable. A plasmon is a collective oscillation of electrons in a metal. At certain resonant frequencies, a photon encountering a metal particle or film can either be strongly absorbed or strongly scattered.

Eli Yablonovitch of the University of California at Berkeley, U.S.A., and Alta Devices (a company investing in a different technology for highly efficient solar cells) is dubious about how much impact plasmonics will have. "The problem is that even the cheapest solar

Doctoral students Qiao Ke, Jin Jin Cong and Yahuitl Osorio Mayon at Australia National University inspect a silicon wafer coated with a diffraction grating fabricated by nano-imprinting. Gratings provide a method of manipulating light at the nanoscale.

cell does a great job collecting light, with typically 99 percent of light collected," he says. (He is referring specifically to traditional thick-film solar cells.) But metal optics can be less efficient. "To be competitive," Yablonovitch says, metal optics "can only tolerate 1 percent losses."

Catchpole, who is developing plasmonic light trapping for solar cells, disagrees. "While standard types of solar cells absorb light well," she says, "many of the newer and potentially cheaper alternatives don't. This is where light trapping has the most potential." In

other words, thin silicon doesn't absorb well at longer wavelengths in the visible spectrum, but it should be able to absorb a lot more if researchers find a clever way to catch the light. She goes on to explain that if you don't design metallic structures carefully, they can be absorbing. But if they are designed right, they can have very low absorption that makes them competitive with other types of materials such as conducting oxides that are used as electrodes for photovoltaics cells.

A lot of plasmonic structures basically scatter light into the absorbing layer. In addition to scattering, some structures also lead to higher electromagnetic fields in the layer (so-called near-field enhancement), but there has been less work on this.

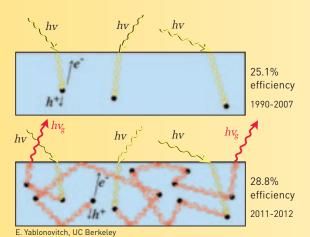
By using a low-loss material like silver to create particles

100 nm in diameter, researchers have learned to optimize forward scattering to get light into the absorbing layer of the solar cell at angles that reduce the chances of it escaping again. By

# "To be competitive, metal optics can only tolerate 1 percent losses."

—Eli Yablonovitch, National Science Foundation

# MAXIMIZING EFFICIENCY: Absorption Isn't the Whole Story



n this schematic, photons from the sun (yellow arrows) enter the solar cell (blue). Some of the photons are absorbed and create pairs of electrons ( $e^-$ ) and holes ( $h^+$ ) that reach the electrodes and thus generate current. In the top cell, which represents cell designs from 1990 to 2007, the internal fluorescence efficiency is poor, limiting the maximum efficiency to 25.1 percent.

The bottom cell, however, has been designed to maximize internally generated photons (red). This internal gas of infra-

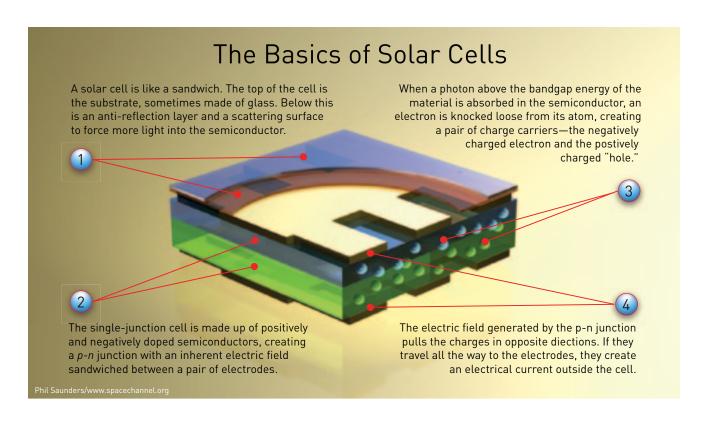
red photons leads to better emission, and thus better voltage.

The highest conversion efficiency reported is 28.8 percent.

As Eli Yablonovitch explains, maximizing light absorption is the optimal strategy for high-efficiency photovoltaics, but a solar cell should also emit light. It's counterintuitive, he says, but a great solar cell should also be a great LED. Yablonovitch is the director of the National Science Foundation's Center for Energy Efficient Electronics Science and a professor at the University of California, Berkeley.

"Up until now, it was understood that, to increase the current from our best solar materials, we had to find ways to get the material to absorb more light," he says. But the power produced by a cell depends on both current and voltage. To increase voltage, "we needed the material to emit more photons outside the solar cell." If a material fluoresces efficiently, then there must be few non-radiative pathways for electrons and holes to recombine, and that's good for generating voltage.

Yablonovitch also says that the optics of a cell is more important than carrier transport. "Non-trivial geometrical optics structures are used in almost every solar cell in the world today." He points out that efficiencies for single-junction GaAs PV cells jumped when the optics improved. "There's room for higher efficiencies, and photonics will play a role." The theoretical limit for a single junction solar cell is 33.5 percent under standard sunlight.

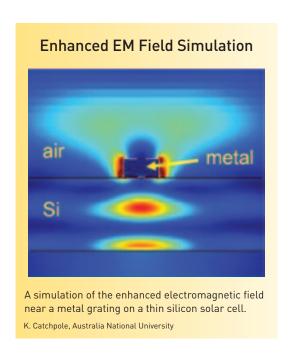


placing the particles close to a high-index semiconductor, the scattered light couples strongly into the semiconductor. Because plasmons decay exponentially with distance from the particle surface, the particles must be within a few tens of nanometers of the semiconductor.

Sometimes the optical structures can also play an electronic role. Recently, Ulrich Paetzold and colleagues from the Juelich Research Center, Germany, described a solar cell in which the plasmonic structure was also the back electrode. The group created silver nanostructures arranged in a square lattice at the back electrode of a 1-µm-thick microcrystalline silicon solar cell. The lattice acted both as a reflection grating and a source of surface plasmons. They found that the structure resulted in better absorption than a comparable flat solar cell for wavelengths from 500 to 1,000 nm. In certain areas, it had an even better short-circuit current density than offered by solar cells with conventional random texture light trapping.

Catchpole's group reported promising results from coating the back surface of a  $2-\mu m$ -thick polycrystalline silicon thin-film cell with a combination of a standard reflective

scattering layer of  ${\rm TiO_2}$  particles and silver nanoparticles. By adding the nanoparticles, their model showed (and the experiment agreed) that most of the long-wavelength light is scattered in an increased angle, such that less can escape.



Catchpole says, "Our paper shows we can use plasmonic particles to change the direction of the light and trap it, and dielectric particles to reflect the light, in a very effective combined structure using simple self-assembly techniques." Simple techniques are always

important for photovoltaics because any commercially competitive technology must produce material on a large, industrial scale.

#### **Nanoshells**

In early 2012, researchers at Stanford University adapted telecommunications nanostructures to use in photovoltaics applications. The team improved absorption in nanocrystalline silicon by creating a layer of tiny hollow

spheres—or nanoshells—on a substrate. Other photonic devices have used similar structures as microresonators, but those designs tend to focus on the wavelength sensitivity and low loss in high-quality structures. For photovoltaics, however, researchers want a structure that can accept and lose light more easily.

The nanoshells catch light from a large range of incident angles and increase the

optical path length. Light gets trapped inside the nanoshells. The longer path length results in more absorption over a broad range of solar wavelengths. The absorption of a single layer of 50-nm-thick spherical nanoshells is equivalent to a 1-µm-thick planar nanocrystalline silicon

film. Further, by depositing two or even three layers of nanoshells atop one another, the team teased the absorption higher still. With a three-layer structure, they were able to absorb 75 percent of incident light in part of the solar spectrum.

In short, the nanoshell design catches much more of the solar spectrum than a flat solar cell, increases the optical path

by about 20 times, and reduces the sensitivity to the light's angle of incidence. Nanoshells use substantially less material, which could dramatically reduce materials usage, weight and processing costs.

The group has not yet demonstrated a higher efficiency cell using this scheme. A recent *Nature Communications* paper by Cui and colleagues provides an experimental demonstration of absorption enhancement, and the nanoshell group is working to show higher conversion efficiency.

Fan's group is interested in understanding the fundamental limit of absorption enhancement in nanophotonic structures and applying such understanding towards the design of advanced solar cells. Meanwhile, Cui's group is experimenting with other devices, including sensors that could benefit from nanoshells.

Fan adds, "The important point about nanophotonic structure is that light management strategy can be applied to many different photovoltaic materials."

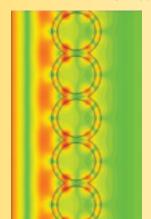
#### Scattering and periodic structures

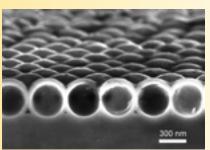
Scattering is important in solar cells, but describing it can be a problem. Catchpole says, "we can't model it well yet, only empirically,"

"Thin-film cell
designs will need
to incorporate
nanophotonic light
trapping in order to
reach their ultimate
efficiency limits."

—Kylie Catchpole, Australia National University

## Silicon Nanoshells





A scanning electron micrograph of a single layer of silicon nanoshells. The hollow shells trap more light to improve absorption efficiency.

Y. Yao, Stanford University

Model of the electric field distribution in an array of nanoshells shows how light approaching from the left is trapped and redirected.

J. Yao, Stanford University



## A Manufacturable 3-D Architecture

Acompany called Solar3D in Santa Barbara, Calif., U.S.A., has designed photovoltaic technology that is 3-D rather than planar. According to the company's website, the design is "inspired by light management techniques used in fiber optic devices," and based on single-crystal silicon. Beyond that, details are scarce. The site states that the design increases the acceptance angles of light entering the cell, traps the light and reduces losses from carrier recombination.

The collected light is then forced into three-dimensional photovoltaic micro-structures beneath the cell surface that trap the light and convert it into electricity.

Thus far, it sounds much like experimental Si nanowire radial *p-n* junction cells. The scanning electron micrograph of a cross-section released by the company, however, shows interestingly angled voids that don't resemble the typical needleshaped gaps from etched silicon.

Company CEO James Nelson won't be specific about the design, citing a pending patent. He does, however, say that it has an open 3-D structure. Inexpensive manufacturability is the goal. In July, the developers made a working prototype.

Nelson expects to release efficiency numbers by the end of 2012. He anticipates that the cell will produce over 25 percent efficiency, which would match that of the highest-efficiency non-concentrated Si cells.

says Catchpole. "So the focus is on more controlled structures."

Periodic nanostructures, on the other hand, are more familiar and well-modeled. They are still being developed in ways that can pay off by improving photovoltaic cell efficiencies. The main types of periodic structures are 1-D multilayer (Bragg) stacks, 2-D gratings and 3-D photonic crystals. By redirecting light in well understood ways, they can be used to trap light within cells.

#### Sunny days ahead

Researchers applying nanophotonics to photovoltaics are pursuing a host of strategies to create better cells. Nanophotonics for photovoltaics is about trapping the light in such a way that the electrical performance of the cell is maintained. Not all proposed structures do this. But one of the new tools we have is making light trapping structures that allow a better quality semiconductor layer, so both light trapping and electrical performance should be improved.

Catchpole concludes, "Thin-film cell designs will need to incorporate nanophotonic

light trapping in order to reach their ultimate efficiency limits."

There is a learning curve for photonics experts to understand the interesting problems in photovoltaics. The OSA meeting on the subject is still of modest size, but the number of papers has grown each year for the past three years—perhaps a promising sign for the future of photovoltaic research.

Yvonne Carts-Powell (yvonne@nasw.org) is a freelance writer specializing in optics and photonics.

#### **REFERENCES & RESOURCES**

- K.R. Catchpole et al. "Plasmonics and nanophotonics for photovoltaics," MRS Bulletin doi: 10.1557/mrs.2011.132/ (2011).
- U.W. Paetzold et al. "Plasmonic reflection grating back contacts for microcrystalline silicon solar cells," Appl. Phys. Lett. doi: 10.1063/1.3657513 (2011).
- ► A. Basch et al. "Combined plasmonic and dielectric rear reflectors for enhanced photocurrent in solar cells," Appl. Phys. Lett., doi: 10.1063/1.4729290 (2012).
- ▶ Y. Yao et al. "Broadband light management using low-Q whispering gallery modes in spherical nanoshells," Nat. Commun. doi: 10.1038/ncomms1664 (2012).