

Plasmonic photovoltaics

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This GCEP project is composed of three sub-projects coordinated by the three PIs. The projects led by Brongersma and Atwater have come to a conclusion in the past year. Polman's project was awarded a no-cost extension. This report first describes two subprojects in Polmans group carried out by PhD students van Lare and Spinelli. Then it describes the collaborative project between Caltech and FOM by PhD student Ferry. Finally, the results from the project at Stanford are reported.

Project 1: Optimized spatial frequencies for light trapping patterns in ultra-thin a-Si:H plasmonic solar cells (Claire van Lare)

In conventional amorphous Si (a-Si:H) cells the thickness is determined by a tradeoff between efficient carrier collection and sufficient light absorption. This limits device efficiency. In this project we studied periodic arrays of metal nanoparticles, either on the front or on the back of the solar cell, and show that light scatters from the arrays into waveguide modes of the solar cell. This results in an increased effective optical path length in the a-Si:H.

We have shown, using finite difference time domain (FDTD) simulations, that a well engineered array of Ag-particles in combination with an ITO layer provides perfect impedance matching between incident light and the aSi:H cell, resulting in a reflectivity similar to that of a standard ITO antireflection coating. Calculations of the of angular distribution of light scattered into the cell show that, depending on the geometry of the particle array, up to 95% of the light is transmitted at angles beyond the critical angle for total internal reflection (14° for a-Si:H/air).

We have used substrate conformal imprint lithography (SCIL) to fabricate nanoparticles on t solar cells. SCIL is an inexpensive, scalable nanoimprint replication technique that reliably reproduces structures with a resolution comparable to e-beam lithography. The a-Si:H cells are grown with 13.56 MHz plasma-enhanced chemical vapor deposition (PECVD). The patterns are tiled across a substrate with repetition to control for inhomogeneities during deposition.

Spectral response (SR) measurements on 150 nm thick n-i-p a-Si:H cells with Ag-particles on the front clearly show strongly enhanced photocurrent in the 650-750 nm spectral range, indicating coupling to optical waveguide modes. Preliminary data show that the photocurrent is enhanced by as much as 24% integrated over the solar spectrum compared to cells without particles, demonstrating efficient light trapping.

For 150 nm thick a-Si:H p-i-n cells with nanoparticles on the back an efficiency enhancement of 10% is observed. Angle-resolved photocurrent spectroscopy is used to characterize the coupling to guided modes. The use of nanoparticles on the back of thin

solar cells, rather than using a closed metal film, reduces carrier recombination, and potentially enhances light trapping. Furthermore it is economically advantageous, since it requires only small amounts of Ag.

The concepts described here are also applicable to other thin film solar cell designs, including polycrystalline Si and CdTe.

Project 2: Light trapping in thin Si solar cells using coupled plasmonic antenna arrays (Piero Spinelli)

We have demonstrate how the incoupling and trapping of light in thin Si solar cells can be improved by using an array of metallic nanoscatterers placed at the surface of the solar cell. The silver antennas act as efficient receivers for a broad spectral band within the solar spectrum and reradiate the incident light over a wide angular range and (for very thin cells) into waveguide modes of the solar cell. In this way the effective optical path length is increased and the photocurrent of the solar cells enhanced. This work enables the design of (ultra-)thin solar cells while maintaining efficient spectral conversion of the sunlight.

Our work is comprised of finite-difference time domain (FDTD) modelling, fabrication of antenna arrays on single-crystal solar cells, optical measurements and photocurrent spectroscopy. First, FDTD simulations were carried out to study the incoupling of light into a Si substrate using a single Ag nanoparticle (diameter 100-300 nm). We find that the scattering and incoupling spectra depend strongly on particle shape and dielectric environment, in particular in the near-field region close to the substrate. Due to the coupling to the high-index substrate, the resonant scattering spectra from these Ag antennas are quite complex. By carrying out a systematic study in which we gradually increase the refractive index of the substrate we identify all scattering peaks and relate them to the (strongly anisotropic) field distribution in the contact area between antenna and substrate. In some geometries we find strong Fano resonance effects that reduce the light incoupling for short wavelengths. Placing the antennas on a thin transparent spacer layer provides further control over the scattering and coupling spectra. We carried out a systematic analysis of all antenna coupling parameters, finding an optimized geometry for 130 nm tall, 200 nm diameter Ag antennas at a 450 nm pitch, placed on a 50 nm Si₃N₄ layer on Si. Most interestingly, we find that this geometry is more efficient for light incoupling than the standard Si₃N₄ anti-reflection coating.

These simulation results are confirmed by optical reflection spectroscopy carried out on 200 μ m thick Si solar cells covered with different Si₃N₄ spacer layers (thickness 20-90 nm). By using electron-beam lithography, we fabricate 80x80 micron arrays of Ag antennas, each array with different antenna diameter and pitch. The optical measurements are in full agreement with the trends found with FDTD simulations regarding particle size, array pitch and Si₃N₄ layer thickness. Most importantly, the optimal antenna array has a reflection coefficient (averaged over the solar spectrum) of only 2%, much better than the standard AR coating. Ag nanoparticle antenna arrays thus provide full impedance matching between sunlight and the semiconductor. The physical insights from this work are applicable to any type of solar cell, including polycrystalline Si, amorphous Si and CdTe thin film solar cells.

Project 3: Light trapping in ultra-thin a-Si:H solar cells (Vivian Ferry)

We investigated the design, fabrication, and simulation of ultrathin film n-i-p a-Si:H solar cells incorporating light trapping plasmonic back reflectors which exceed the performance of n-i-p cells on randomly textured Asahi substrates. The periodic patterns are made via an inexpensive and scalable nanoimprint method, and are structured directly into the metallic back contact. Compared to reference cells with randomly textured back contacts and flat back contacts, the patterned cells exhibit higher short-circuit current densities and improved overall efficiencies than either reference case. Angle-resolved photocurrent measurements confirm that the enhanced photocurrents are due to coupling to waveguide modes of the cell. Electromagnetic modeling is shown to agree well with measurements, and used to understand further details of the device.

In this project we developed several new insights into the nature of light trapping in a highly efficient ultra-thin amorphous Si:H solar cell. The three key new developments are:

Insight into role of randomness vs order in light trapping nanostructures: Many papers have now been written about light trapping in thin solar cells and enhanced photocurrents. However what has been lacking to date is fundamental understanding of the relation between the observed photocurrent enhancements and the spatial correlations and surface topography of periodic and random nanostructured scatterers. In this project, we present for the first time a systematic study of this relation, involving more than 1000 solar cells, establishing a direct relation between the spatial coherence spectral density an measured and simulated photocurrent spectra.

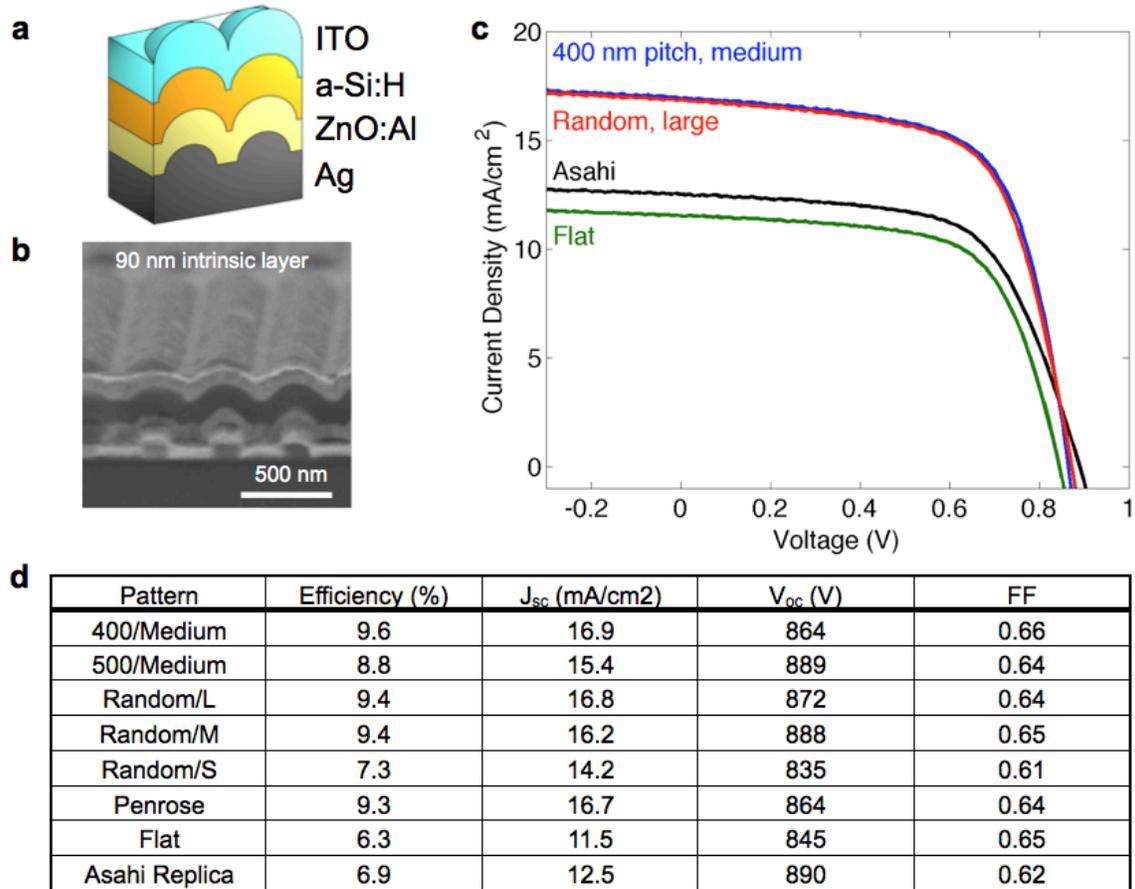
Simultaneous rear reflector-enhanced red response and front surface-enhanced blue response. The backside reflector in our work is a randomly nanopatterned reflector with power spectral density such that light preferentially couples to waveguide modes of the solar cell over a broad spectral range in the red/near-infrared. At the same time, the front surface topography is composed of arrays of weakly coupled Mie resonators that strongly enhance the light coupling into the cell and redirect light into localized modes of the cell over a broad band in the UV/blue spectral range.

A highly efficient extremely thin a-Si:H cell. In our new design, both these geometries are combined in the same cell, leading to the realization of an extremely thin solar cell (90 nm intrinsic Si layer thickness) with enhanced spectral response in both the UV/blue and red/infrared solar spectral bands. We demonstrate a power conversion efficiency of over 9.5% which is approaching the single-junction cell record efficiency for a-Si:H of 10.2%, but with a cell approximately one-third as thick as the record cell.

In our work we introduce for the first time the concept of weakly coupled Mie resonators that are integrated with the surface topography of the cell. These resonantly absorb light and redirect it into the cell, thereby effectively enhancing the incoupling of light into the device. These scatterers avoid the need of macroscopic surface texture which is very difficult to apply to ultra-thin solar cells.

Our work is enabled by the recent availability of soft imprint lithography, which makes it possible, for the first time, to fabricate engineered random arrays of nanopatterns over large areas. Indeed, our new design is easily scalable to the very large areas required for solar cell manufacturing.

Ultra-thin film solar cells offer many advantages over their thick film counterparts, including reduced fabrication costs, higher open circuit voltages, less dependence on inabundant elements, and improved stability under light illumination (for a-Si:H). We demonstrate in this project that our new design can effectively reduce the cell thickness nearly 3-fold (from 250 to 90 nm intrinsic layer thickness) while maintaining an efficiency close to the world for a-Si:H. While the spatial correlation design concepts are presented and implemented here for a-Si:H, the physical concepts are potentially applicable to many other solar cell technologies.



Current-voltage characteristics of nanopatterned cells. The cells are conformally deposited over the patterned substrate, as shown schematically in **a** and in SEM cross section (5° angle) in **b**. The maximum particle diameter in the backpattern was chosen so that nanostructures in the ITO top layer would touch without overlap. **c** Current-voltage measurements for the best-efficiency cells on the substrate with 90 nm intrinsic layers. The optimized periodic pattern and the pseudo-random pattern have efficiencies of 9.6% and 9.4%, respectively. **d** Electrical characteristics of highest-efficiency cells.

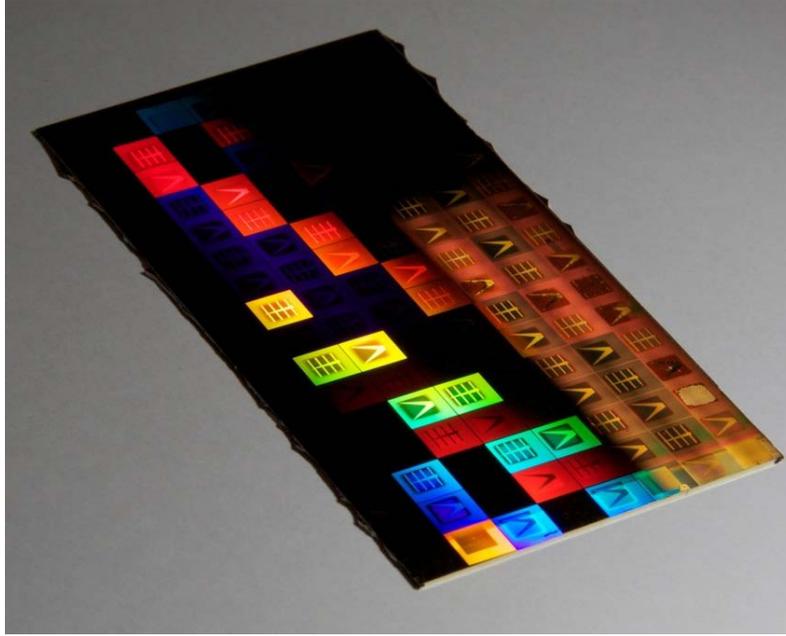
Workshop organized at national FOM conference (Veldhoven, January, 2011)

Topic: Advanced silicon solar cells: Thin solar cells may enable the generation of electricity from the sun at low costs. To achieve this goal it is essential to achieve, in one design: efficient light trapping, efficient carrier collection and minimized surface recombination. This workshop addressed recent insights and advances in this field, including the use of advanced heterojunctions to enhance carrier collection at higher potentials. Speakers were:

1. Silicon based hetero-junction solar cells – from wafers to thin-films - Bernd Rech (Helmholtz Institute, Berlin)
2. Light trapping in ultra-thin Si solar cells - Vivian Ferry (AMOLF/CALTECH/GCEP)
3. Field-effect passivation of silicon surfaces by ultrathin negative-charge dielectric films for high-efficiency solar cells - Erwin Kessels (TUE)
4. High-efficiency amorphous Si/crystalline Si solar cells - Bart Geerligs (ECN)

Publications of Polman and Atwater group on this GCEP project since April 30, 2010

1. *Controlling Fano lineshapes in plasmon-mediated light coupling into a substrate*, P. Spinelli, C. van Lare, E. Verhagen and A. Polman, *Optics Express* **19**, A303 (2011)
2. *Resonant SPP modes supported by discrete metal nanoparticles on high-index substrate*, F.J. Beck, E. Verhagen, S. Mokkaapati, A. Polman, and K.R. Catchpole. *Optics Express* **19**, A146 (2011)
3. *Resonant nano-antennas for light trapping in plasmonic solar cells*, S. Mokkaapati, F.J. Beck, R. de Waele, A. Polman and K. R. Catchpole, *J. Phys. D: Appl. Phys.* **44**, 185101 (2011)
4. *Optical impedance matching using coupled metal nanoparticle arrays*, P. Spinelli, M. Hebbink, R. de Waele, L. Black, F. Lenzmann and A. Polman, *Nano Lett.* **11**, 1760 (2011)
5. *Light trapping in thin-film plasmonic solar cells*, V.E. Ferry, M.A. Verschuuren, H.B.T. Li, E. Verhagen, R.J. Walters, R.E.I. Schropp, H.A. Atwater and A. Polman, *Proc. 25th EUPVSC Conference, Valencia, September 6-10, 2010*, pp. 10-14
6. *Plasmonic light trapping for thin film a-Si:H solar cells*, V.E. Ferry, M.A. Verschuuren, H.B.T. Li, E. Verhagen, R.J. Walters, R.E.I. Schropp, H.A. Atwater and A. Polman, *Proc. 35th IEEE Photovoltaic specialist conference, Hawaii, USA, June 20-25, 2010*, pp. 760-765



Photograph of plasmonic solar cells made in this GCEP project.

Project 4: Design of non-periodic plasmonic structures for light trapping (Brongersma group)

Commercial solar cells typically utilize some form of surface texturing to trap light in a high refractive index semiconductor layer. Many of the applied textures exhibit a certain degree of randomness. Such textures appear better than periodic structures at scattering broadband sunlight into waveguided modes of a high index semiconductorⁱ. Despite their importance, a detailed understanding of the design of aperiodic light trapping structures is not yet available. This is in part because electromagnetic simulations of their behavior are complicated by the fact that a wide variety of materials and length-scales are important. Light trapping can involve nanoscale high index dielectric and semiconductor structures or nanoscale metallic structures with a large negative value of the dielectric constant. Also collective effects that result from the interaction of large number of nanoscale building blocks placed in an array needs to be taken into account. Obviously simple ray-tracing codes do not suffice and often one ends up modeling periodic structures for which boundary conditions can be applied, reducing computation cost.

As part of our proposed effort, we have started exploring the ability of aperiodic, nanometallic (i.e. plasmonic) nanostructures for light trapping. Such structures can be deposited on top of a flat solar cell, potentially embedded into a transparent conductive oxide. This approach to light trapping may be preferred over roughening the semiconductor surface, which known to cause degradation in the electrical performance. It is already well-established that periodic plasmonic structures can provide a substantial increase in the light absorption at specific wavelengths.^{ii,iii,iv} Unfortunately, periodic structures such as a grating, give rise to efficient waveguide coupling at a very limited set of well-defined wavelengths. Such coupling occurs when the k -vector of the grating (i.e. $2\pi/\text{period}$) matches a propagation constant of one of the waveguide modes supported by the semiconductor layer. Aperiodic structures enable more broadband coupling by

providing more spatial frequencies (i.e k-vectors) for coupling. It is thus important to evaluate to degree of randomness that is needed for optimum performance. Perfectly random may provide an ability to couple light at wavelengths where the semiconductor material does not absorb at the expense of the coupling efficiency at wavelength where coupling is desirable. There are no systematic studies that carefully compare the light trapping performance of periodic, different types of non-periodic, and random structures. Figure 1 shows a full-field simulation of the spectral contributions to the short-circuit current that we expect for 1) a bare, 50-nm-thick Si slab, 2) the same slab with periodic grating of 300 nm period, and 3) the same slab with a randomized grating in which the constituent metallic bars were randomly displaced from their lattice positions. It is clear that both the periodic and randomized gratings enhance the short circuit current over a large part of the spectrum. The periodic grating produces strong peaks and the randomized structure provides a more broadband absorption enhancement. To further enhance absorption, it is important to tailor the spatial frequencies present in the coupling structures to maximize coupling near the peak of the solar spectrum or near the bandedge of the semiconductor where its absorption is weakest. This will be pursued in future studies.

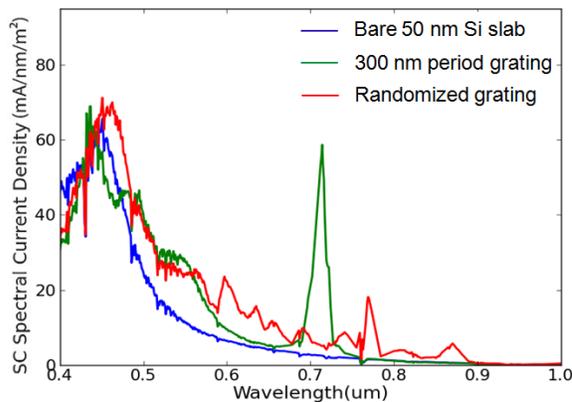


Figure 1. Full-field electromagnetic simulation of the short circuit current spectra of 1) a bare, 50-nm-thick Si slab, 2) the same slab with periodic grating of 300 nm period, and 3) the same slab with a randomized grating in which the constituent metallic bars were randomly displaced from their lattice positions. The simulations were based on the finite-difference time-domain technique that can utilize real/experimental values for the optical properties of the semiconductors and metals.

ⁱ Yablonovitch, E. *J. Opt. Soc. Am.* **1982**, 72, (7), 899-907.

ⁱⁱ “Design of Plasmonic Thin-Film Solar Cells with Broadband Absorption Enhancements,” Ragip A. Pala, Justin White, Edward Barnard, John Liu, and Mark L. Brongersma, *Adv. Mater.* **21**, 3504-3509 (2009).

ⁱⁱⁱ “Improved Red-Response in Thin Film a-Si:H Solar Cells with Soft-Imprinted Plasmonic Back Reflectors,” Vivian E. Ferry, Marc A. Verschuuren, Hongbo B. T. Li, Ruud E. I. Schropp, Harry A. Atwater, and Albert Polman, *Appl. Phys. Lett.* **95**, 183503 (2009).

^{iv} “Plasmonics for improved photovoltaic devices,” Harry Atwater and Albert Polman, *Nature Materials* **9**, 205 (2010).