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Roadmap on optical energy conversion

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Svetlana Boriskina *et al,* commissioned for *Journal of Optics*

Abstract

For decades, progress in the field of optical (including solar) energy conversion was dominated by advances in the conventional concentrating optics and materials design. In recent years, however, conceptual and technological breakthroughs in the fields of nanophotonics and plasmonics combined with better understanding of the thermodynamics of the photon energy conversion processes re-shaped the landscape of energy conversion schemes and devices.

Nanostructured devices and materials that make use of size quantization effects to manipulate photon density of states offer a way to overcome the conventional light absorption limits. Novel optical spectrum splitting and photon recycling schemes reduce the entropy production in the optical energy conversion platforms and boost their efficiencies. Optical design concepts are rapidly expanding into the infrared energy band, offering new approaches to harvest waste heat, reduce the thermal emission losses, and achieve non-contact radiative cooling of solar cells as well as of optical and electronic circuitry. Light-matter interaction enabled by nanophotonics and plasmonics underlie the performance of the third-and fourth-generation energy conversion devices, including up- and down-conversion of photon energy, near-field radiative energy transfer, and hot electron generation and harvesting. Finally, the increased market penetration of alternative solar energy conversion technologies amplifies the role of cost-driven and environmental considerations.

This roadmap on optical energy conversion provides a snapshot of the state-of-the art in optical energy conversion, remaining challenges, and most promising approaches to address these challenges. Leading experts authored 19 focused short sections of the roadmap, where they share their vision on a specific aspect of this burgeoning research field. The roadmap opens up with a tutorial section, which introduces major concepts and terminology. It is our hope that the roadmap will serve as an important resource for the scientific community, new generations of researchers, funding agencies, industry experts and investors.

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Contents

1. Tutorial: thermodynamics of light and conventional limits of photon energy conversion

– Svetlana V Boriskina
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Thermodynamic properties of photon systems and their interaction with matter define efficiency limits of light energy conversion schemes[1,2]. Photons can be uniquely characterized by their energy $\hbar\omega = hc/\lambda$, momentum $\hbar\mathbf{k}$, and angular momentum, which e.g. in the case of plane wave in free space defines light polarization ($h = 2\pi\hbar$ is the Planck's constant, λ, ω are photon wavelength and angular frequency, and $\mathbf{k}$ is the wavevector)[3,4]. In the interactions of photons with matter – such as light emission or absorption – the concept of temperature T is introduced to account for energy conservation. Some types of interactions such as fluorescent emission or Bose-Einstein condensation[5] require adding a concept of photon chemical potential μ to account for the particle number conservation[6].

The photon density of states (DOS) defines the number of states in the momentum space between k and $k + dk$ per unit volume and solid angle Ω that are available for a photon to occupy in 3D space as: $D(k)dk = k^2\Omega dk/(2\pi)^3$ (Fig. 1a). DOS as a function of photon energy is expressed via the photon dispersion relation: $D(\omega) = \Omega/(2\pi)^3 \cdot k^2(\omega) \cdot dk/d\omega$ [3,4]. For plane waves of both polarizations in isotropic bulk dielectric with refractive index n and $\Omega = 4\pi$, $D = \omega^2 n^3/\pi^2 c^3$. Low bulk photon DOS is often a limiting factor in manipulating and enhancing absorption and emission processes. However, as DOS is inversely proportional to the photon group velocity $\upsilon_g = (dk/d\omega)^{-1}$, trapped modes with flat dispersion can have DOS significantly exceeding that of bulk materials, especially in the near field [see section 16][7–12].

As gauge bosons for electromagnetism, photons obey **Bose-Einstein statistics**, with the mean occupation numbers in thermal equilibrium defined as $\tilde{N}(\omega, T, \mu) = (\exp((\hbar\omega - \mu)/k_B T) - 1)^{-1}$, where k_B is the Boltzmann constant and $\mu = 0$ for blackbody radiation (Fig. 1a,b)[2–4]. The electromagnetic energy density of radiation in a material per unit time and angle is defined via the well-known Planck's formula as $U = \hbar\omega \cdot N(\omega, T, \mu) \cdot D(\omega)d\omega$ [1,2]. It can be tailored not just by the temperature as typical for the blackbody radiation but also by the photon DOS and [see sections 13,15-19]. In turn, light intensity (power per unit area) is $I = {}_g \times U$ [13] (Fig. 1b). Integration of I over the whole frequency and angular range yields optical energy flux through a unit surface area per unit
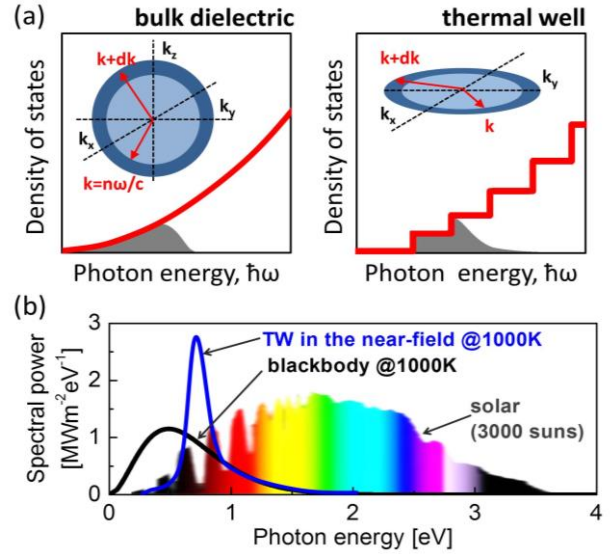

Figure 1 – (a) Photon DOS (red lines) in isotropic bulk dielectrics (left) and dielectric thin films, which act as thermal analogs of quantum wells[10] (right). Shaded grey areas: thermal distribution of photons shaped by the electromagnetic potential. Insets: iso-energy surfaces (contours) in the photon momentum space. Sub-wavelength-scale particles, thin metal films, photonic crystals, and metamaterials also strongly modify DOS[9], especially in the near field[12]. (b) Power flux spectra of solar photons as well as photons emitted by the 1000K blackbody probed in the far field (black) and by a thin-film thermal well probed in the near-field[10] (blue). Although the sun emits as a blackbody at $T_s \sim 6000K$, solar power flux is reduced due to small angular range of terrestrial illumination and atmospheric attenuation.

time, which for the blackbody source at temperature T in free space equals T^4 (is the Stefan–Boltzmann constant). The ratio of light intensities in an absorbing medium and free space defines the **absorption limit**, which in the case of bulk dielectric with a back reflector and isotropic light escape has a well-known value $4n^2$ [13,14]. However, high-DOS [sub-]wavelength-scale absorbers can exceed this limit.[10,11] They can have absorption cross-sections larger than geometrical ones[9,15] [see section 13], and thus feature higher than blackbody emittance[16].

Light can also be characterized by the **entropy of photon gas**, with the entropy flux defined generally as $S(T, \mu) = k_B \iint \upsilon_g \cdot D(\omega) \cdot [(1+N)\ln(1+N) - N\ln N]d\omega d\Omega$ [2,17]. At the thermal equilibrium, the entropy reaches its maximum and the photon occupation numbers obey the familiar Bose-Einstein distribution, $N = \tilde{N}$. The entropy flux of a blackbody source equals $4\sigma/3 \cdot T^3$; and this value decreases if frequency and/or angular ranges shrink, tending to zero for a monochromatic directional radiation (e.g. laser beam). The introduction of the concept of photon entropy[17] helped to resolve

the controversy about the thermodynamic second law violation in optical refrigeration (i.e., anti-Stokes fluorescent cooling)[18,19]. It is also at the core of efficiency limits of the photon energy conversion[20].

Fundamental efficiency limits for conversion of the photon energy into useful work stem from the laws of thermodynamics and quantum mechanics. The conversion efficiency of any photon energy conversion platform (Fig. 2a) can be calculated in a general form by balancing the energy and entropy flows:

$$\eta = \frac{W}{I_s} = 1 - \frac{1}{I_s}\left[I_r(T_a) + T_c\left[S_s(T_s) - S_r(T_a) + S_g\right]\right].$$ When

both the source and the absorber emit as blackbodies with $\mu = 0$ and no entropy is generated in the engine, the above formula reduces to the **Landsberg efficiency**[21], which represents an upper limit of the solar energy conversion efficiency. Landsberg efficiency reaches maximum value at $T_a = T_e = T_c$ (93.3% if $T_a = 300K$ and $T_s = 6000K$). A more conventional **Carnot efficiency**[22] $\eta = 1 - T_c/T_a$ is obtained if there is no radiative energy exchange between the source and the absorber (95% if $T_a = T_s$ and $T_c = 300K$). Both Landsberg and Carnot limits assume complete reversibility, while operation of realistic photon conversion platforms involves irreversible thermodynamic processes such as photon absorption and charge carrier thermalization, and is accompanied by entropy creation [see section 20]. Absorption and emission properties of realistic converters may also differ significantly from those of a blackbody. Finally, operation at the efficiency limit typically means that the power is extracted infinitely slowly, while the maximum-power-out efficiency can be found by solving $dW(\eta)/d\eta = 0$.

For example, maximum-power-generation efficiency of a photovoltaic (PV) cell can be obtained from the general formula by assuming entropy production in the cell due to charge carriers thermalization with the crystal lattice as well as particle number conservation and fluorescent emission with the chemical potential equal to the applied voltage ($= eV$). The resulting limiting efficiency is known as the **Shockley-Queisser limit**[23,24], which is shown in Fig. 2b for the case of a single-junction PC cell with a threshold absorption energy corresponding to the width of the electron bandgap of the cell material. It is also known as the **detailed balance limit**. Higher efficiency has been theoretically predicted[25] for the regime of operation when the photo-excited charge carriers are extracted after they thermalize between themselves yet prior to their thermalization with the lattice, which reduces entropy creation (Fig. 2b). While **hot-carrier photon energy converters** with high efficiencies have not yet
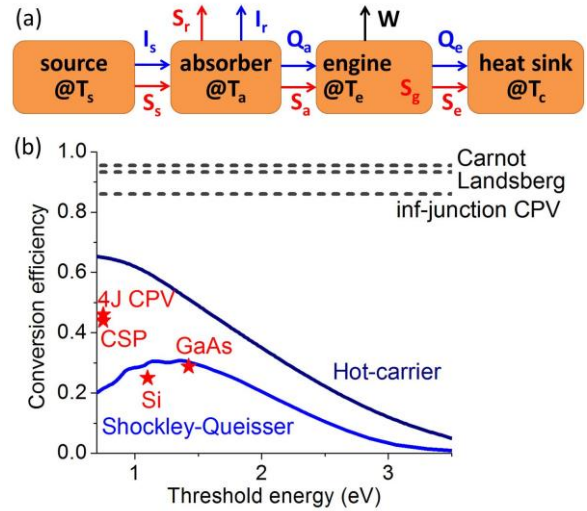

Figure 2 – (a) A general schematic of a solar energy converter. Blue arrows – energy fluxes in the form of radiation (*I*) or heat (*Q*), red arrows – corresponding entropy fluxes through the converter. Irreversible entropy (S_g) can be generated in the engine. (b) Fundamental limits for photon energy conversion efficiency. Shockley-Queisser limit is plotted for an ideal single-junction PV cell at *T*=300*K* under one-sun illumination. For the infinite number of PV junctions and full solar concentration it reaches 86.6% (dashed line)[24] [see sections 11-13]. Hot-carrier efficiency limit[25] is shown for an ideal cell with electron temperature *T*=3000*K* and lattice temperature *T*=300*K* under one sun illumination.

been realized, there is promising ongoing work in this direction that focuses on quantum confinement effects and plasmonics [see sections 5,6,9,13].

Concluding Remarks – All practical realizations of photon energy converters operate at lower efficiencies that their theoretical limits[26] due to design and material imperfections (Fig. 2b) . However, deep understanding of the origin and constraints of fundamental limits guides future research and development in the area of light energy conversion[27]. In particular, advanced material developments and optimized optical designs have recently propelled some technologies (e.g., GaAs PV cells[28]) to the brink of reaching their theoretical limits of operation [sections 2-5], and there is still plenty of space at the top of the efficiency scale (Fig. 2b). Many opportunities still exist not only for material designers [see sections 3,5-10,14] but also for optical scientists and engineers to reach and overcome the efficiency limits [see sections 2-4, 9-19]. Novel optical concepts and schemes for light concentration, photon trapping, optical spectrum splitting, and material emittance modification offer new insights and yield new technological solutions for solar and thermal energy harvesting. These insights will also benefit other fields such as solid state and advanced incandescent lighting, optical refrigeration, waste heat harvesting and radiative cooling just to name a few.

References

[1]   (1)   Planck, M. *The Theory of Heat Radiation*; 1914.

[2]   (2)   Landau, L.; Lifshitz, E. *Statistical Physics, Part 1*; Institute of Physical Problems, USSR Academy of Sciences: Moscow, 1980.

[3]   (3)   Levi, A. F. J. *Applied Quantum Mechanics*; 2006.

[4]   (4)   Chen, G. *Nanoscale Energy Transport and Conversion: A Parallel Treatment of Electrons, Molecules, Phonons, and Photons*; Oxford University Press, USA, 2005.

[5]   (5)   Klaers, J.; Schmitt, J.; Vewinger, F.; Weitz, M. Bose-Einstein Condensation of Photons in an Optical Microcavity. *Nature* **2010**, *468*, 545–548.

[6]   (6)   Wurfel, P. The Chemical Potential of Radiation. *J. Phys. C Solid State Phys.* **1982**, *15*, 3967.

[7]   (7)   Stuart, H. R.; Hall, D. G. Thermodynamic Limit to Light Trapping in Thin Planar Structures. *J. Opt. Soc. Am. A* **1997**, *14*, 3001–3008.

[8]   (8)   Callahan, D. M.; Munday, J. N.; Atwater, H. A. Solar Cell Light Trapping beyond the Ray Optic Limit. *Nano Lett.* **2012**, *12*, 214–218.

[9]   (9)   Boriskina, S. V.; Ghasemi, H.; Chen, G. Plasmonic Materials for Energy: From Physics to Applications. *Mater. Today* **2013**, *16*, 375–386.

[10]   (10)   Tong, J. K.; Hsu, W.-C.; Huang, Y.; Boriskina, S. V.; Chen, G. Thin-Film "Thermal Well" Emitters and Absorbers for High-Efficiency Thermophotovoltaics. *Sci. Reports* **2015**, *5*, 10661.

[11]   (11)   Yu, Z.; Raman, A.; Fan, S. Fundamental Limit of Nanophotonic Light Trapping in Solar Cells. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 17491–17496.

[12]   (12)   Joulain, K.; Mulet, J.-P.; Marquier, F.; Carminati, R.; Greffet, J.-J. Surface Electromagnetic Waves Thermally Excited: Radiative Heat Transfer, Coherence Properties and Casimir Forces Revisited in the near Field. *Surf. Sci. Reports* **2005**, *57*, 59–112.

[13]   (13)   Yablonovitch, E. Statistical Ray Optics. *J. Opt. Soc. Am.* **1982**, *72*, 899–907.

[14]   (14)   Wurfel, P. *Physics of Solar Cells: From Principles to New Concepts*; WILEY-VCH Verlag GmbH &Co. KGaA: Weinheim, 2005.

[15]   (15)   Bohren, C. F. How Can a Particle Absorb More than the Light Incident on It? *Am. J. Phys.* **1983**, *51*, 323–327.

[16]   (16)   Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Weinheim, Germany, 1983; Vol. 98.

[17]   (17)   Landau, L. On the Thermodynamics of Photoluminescence. *J. Phys.* **1946**, *10*, 503–506.

[18]   (18)   Pringsheim, P. Zwei Bemerkungen Über Den Unterschied von Lumineszenz Und Temperaturstrahlung. *Z. Phys.* **1929**, *57*, 739–746.

[19]   (19)   Sheik-Bahae, M.; Epstein, R. I. Optical Refrigeration. *Nat. Photonics* **2007**, *1*, 693–699.

[20]   (20)   Green, M. Energy, Entropy and Efficiency. In *Third Generation Photovoltaics*; Kamiya, T.; Monemar, B.; Venghaus, H., Eds.; Springer Berlin Heidelberg, 2006; Vol. 12, pp. 21–34.

[21]   (21)   Landsberg, P. T.; Tonge, G. Thermodynamic Energy Conversion Efficiencies. *J. Appl. Phys.* **1980**, *51*, R1–R20.

[22]   (22)   Carnot, N. L. S. *Reflections on the Motive Power of Heat*; 1824.

[23]   (23)   Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of P-N Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510 – &.

[24]   (24)   Henry, C. H. Limiting Efficiencies of Ideal Single and Multiple Energy Gap Terrestrial Solar Cells. *J. Appl. Phys.* **1980**, *51*, 4494–4500.

[25]   (25)   Ross, R. T.; Nozik, A. J. Efficiency of Hot-Carrier Solar Energy Converters. *J. Appl. Phys.* **1982**, *53*, 3813.

[26]   (26)   Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. Solar Cell Efficiency Tables (Version 45). *Prog. Photovoltaics Res. Appl.* **2015**, *23*, 1–9.

[27]   (27)   Boriskina, S. V.; Tong, J. K.; Ferry, V. E.; Michel, J.; Kildishev, A. V. Breaking the Limits of Optical Energy Conversion. *Opt. Photonics News* **2015**, 50–53.

[28]   (28)   Miller, O. D.; Yablonovitch, E.; Kurtz, S. R. Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit. *IEEE J. Photovoltaics* **2012**, *2*, 303–311.

2. The commercial push of silicon photovoltaics to high efficiency – Martin A Green

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Status – Solar cells seem destined to play a large role in future energy supply, due to cell prices decreasing by a factor of 8 since 2008 and the installed photovoltaic system capacity increasing by a factor of 50 over the last decade. Overall manufacturing costs are continuing to decrease by circa 10%/year due to a combination of decreasing prices of purified polysilicon source material and silicon wafers, increased manufacturing volumes and increasing energy conversion efficiency [1]. Increasing the latter efficiency not only reduces costs per unit power rating by increasing power output for a given investment in material and processing costs, it also similarly leverages transportation and installation costs when the solar modules are subsequently put into use.

The cell structure that has been produced in the highest volume to date is the Al-BSF (aluminium back surface field) cell shown uppermost in Fig. 1 [1,2]. A boron-doped, p-type wafer presently about 180 microns thick is the starting point in the manufacture of these cells. After cleaning and surface texturing, these wafers are diffused with phosphorus to form the n^+ region of a p-n junction. The metal contacts are then screen-printed, with most of the rear covered by a screened Al-based paste. During firing, this layer alloys with the silicon to form an Al-doped p^+ region at the rear, known as the Al-BSF.

This fabrication sequence became the standard production approach in the 1980s with over 200 GW of cells based on this approach now deployed. Ongoing improvements in the pastes and processing sequences used in cell fabrication has seen steady increases in cell performance to the stage where manufacturers can routinely manufacture cells in the 17-18% efficiency range on multicrystalline substrates in 2015, increasing to 18-19% on better quality monocrystalline substrates [1].

Current and Future Challenges – The performance-limiting feature of the cell has now become the Al-BSF region. To progress past the 20% efficiency mark in production, manufacturers are looking to high efficiency cell structures that overcome this limitation.

Advances in Science and Technology to Meet Challenges – The challenge of increasing cell efficiency considerably above 20% has been met by three vastly different cell structures, also shown in Fig.1, that have all now demonstrated efficiencies of 25% or higher in the laboratory [3] and are being fabricated in increasing volume commercially.
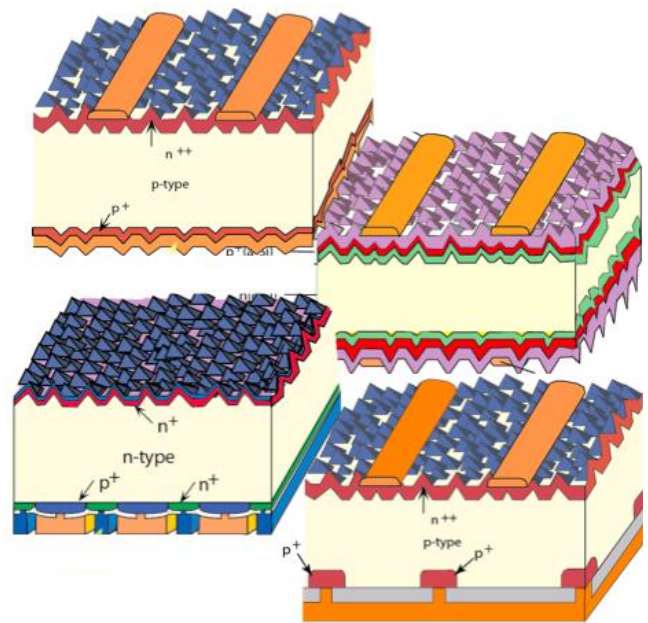

Figure 1 – Commercial silicon solar cells. From top to bottom are shown the standard aluminium back surface field (Al-BSF) cell, the heterojunction (HJT) cell, the rear-junction (Rear J) cell and the Passivated Emitter and Rear Cell (PERC).

The first to reach 25% efficiency [4] was the Passivated Emitter and Rear Cell (PERC) shown lowermost in Fig. 1, first reported in 1989 [5]. Although the most recent to be introduced into large-scale commercial production, PERC cells have already established the strongest commercial position (Fig. 2). In the structure, the Al-BSF is replaced by a more sophisticated rear contacting approach that not only reduces detrimental carrier recombination at the cell rear but also improves reflection of weakly absorbed light reaching this surface. Industry consensus is that, by 2020, the PERC cell will displace the Al-BSF approach as the dominant commercial technology [1], as indicated in Fig. 2. The strength of the technology is its robustness, being suitable for improving performance of both low and high-quality silicon wafers, giving it an advantage over the other two technologies to be described.

The second cell structure, reaching 25% efficiency in 2014 [3], is the rear junction solar cell, shown second lowermost in Fig. 1. This structure was first suggested in 1977 [6] with the first efficient devices reported in 1984 [7]. Close to 1 GW of these cells were sold in 2014 representing about 2.3% of the total market. Industry consensus is that this market share is poised to increase, although this likely depends upon the availability of high-quality, monocrystalline n-type wafers at lower cost than presently available [1]. Cells have an unusual geometry where both polarity contacts are located on the rear, unilluminated cell surface. This

has the advantage of avoiding metal contact shading the front surface, eliminating one of the obvious losses of traditional cells. Since most light is absorbed close to entry at the top surface, photo-generated carries have to diffuse across the wafer to be collected at the rear, making the structure suitable only for good quality wafers.
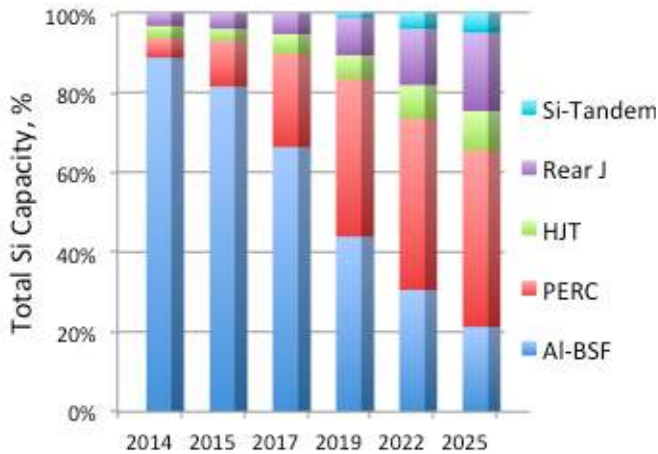

Figure 2 – Industry consensus on the present and future market share of the different silicon cell technologies of Figure 1 (data extracted from Ref. [1]).

The final cell structure to have given efficiency close to 25% is the heterojunction cell approach pioneered by Sanyo (now Panasonic) [8], taking advantage of the company's considerable prior experience with hydrogenated amorphous silicon (a-Si:H) thin-film cells. The high atomic percentage of hydrogen in the a-Si:H imparts properties completely different from crystalline silicon (c-Si) including a wider bandgap (1.7eV versus 1.1eV) and electron affinity about 0.1 - 0.2eV lower. An important feature is inclusion of a very thin layer of undoped, intrinsic a-Si:H between the c-Si wafer and the oppositely doped a-Si:H layers deposited on either side of the wafer. Given the higher bandgap of the a-Si:H regions, essentially all recombination occurs in the pristine c-Si wafer or at its interfaces with the intrinsic a-Si:H layer. The latter turns out to be very low, resulting in the highest open-circuit voltage of any c-Si cell technology. Combining with the rear junction approach recently increased record Si-cell efficiency to 25.6% [3,9].

Concluding Remarks – These high efficiency cell technologies will enable the ongoing incremental improvement in commercial silicon cell efficiency to the best laboratory values of circa 25%, with 29% a fundamental limit. The most likely route to allow significant progress beyond this point is by going to a tandem cell approach, where a higher bandgap cell is monolthically integrated on top of the c-Si cell. Some

recent success in this direction has been obtained by combining with perovskite solar cells [10] [see section 3], although the present lack of perovskite cell stability prevents serious consideration for commercial use. Some industry participants however rather optimistically believe that such tandem technology may be ready for commercial application by 2019 (Fig. 2).

References
[1] International Technology Roadmap for Photovoltaic (ITRPV), Sixth Edition, April 2015 (www.itrpv.net).
[2] Neuhaus D.-H.and Münzer A 2007 Industrial silicon wafer solar cells. *Adv. OptoElectron* doi:10.1155/2007/24521.
[3] Green M A et al. 2015 Solar Cell Efficiency Tables (Version 45) *Progress in Photovoltaics* 23 1-9.
[4] Green M A 2009 The Path to 25% Silicon Solar Cell Efficiency: History of Silicon Cell Evolution *Prog. in Photovoltaics* 17 183-189.
[5] Blakers A W *et al.* 1989 22.8% Efficient Silicon Solar Cell *Appl. Phys. Lett.,* 55 1363-1365.
[6] Lammert M D and Schwartz R J 1977 The interdigitated back contact solar cell: A silicon solar cell for use in concentrated sunlight *IEEE Trans. Electron Devices* 24 337-342.
[7] Swanson, R M *et al*. 1984 Point-Contact Silicon Solar-Cells *IEEE Trans. Electron Devices* 31 661-664
[8] Taguchi M *et al.* 2000 HIT^{TM} cells—high-efficiency crystalline Si cells with novel structure *Progress In Photovoltaics* **8** 503–513.
[9] Masuko K et al. 2014 Achievement of more than 25% conversion efficiency with crystalline silicon heterojunction solar cell *IEEE Journal of Photovoltaics* **4** 1433-1435.
[10] Mailoa, J P *et al.* 2015 A 2-terminal perovskite/silicon multijunction solar cell enabled by a silicon tunnel junction *Appl. Phys. Lett.* **106** 121105.

3. Optics and nanophotonics for silicon cells and silicon-based tandem cells – Kylie Catchpole

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Status – Currently, about 90% of the photovoltaic market is based on crystalline Si solar cells. Si is the third most abundant element on Earth and has a near ideal band gap energy for maximizing the efficiency of a single junction solar cell. c-Si solar cells have now exceeded efficiencies of 25% in the laboratory, and silicon modules have reached an efficiency of over 22% [see section 2]. In order to take advantage of the decades of development of silicon and massive economies of scale that have been achieved, it makes sense to push the technology to the highest efficiencies possible. To do this, it is essential that optical losses are minimised. Even when this has been achieved, however, Si solar cells are limited to an efficiency of about 27% by Auger recombination. Because of this, there has been increasing interest in combining emerging materials such as perovskites with silicon to form high efficiency tandems [see also sections 11,13]. For such tandems, sophisticated designs that minimize optical loss are crucial in order to go beyond the break-even point, and to realize the potential of the high bandgap material.

Optical loss mechanisms in solar cells are due to reflection from the front surface, incomplete absorption and escape from the solar cell, and parasitic absorption. All of these need to be addressed in order to reach the maximum efficiencies. Incomplete absorption is important when the solar cell is thin compared to the absorption length of light. This is relevant as silicon wafers become thinner in order to reduce costs, and for perovskite materials, which can have relatively low diffusion lengths. Reflection control is necessary for all types of solar cells, but is particularly important for multi-crystalline cells where anisotropic wet etching cannot be used to create pyramids.

Nanophotonics, which involves structures on the scale of the wavelength of light, is an important approach in the optical engineering of solar cells, because it allows a level of control that cannot be achieved with conventional geometrical optics. Nanophotonic techniques can be large area and potentially cheap. To date many different approaches have been used for reducing reflection and increasing light trapping in solar cells, including etched surfaces, plasmonic nanoparticles and reflectors, diffuse reflectors and photonic crystals. For a more detailed overview of this work, see [1].

Current and Future Challenges – The emergence of the perovskites has led to the possibility of cheap tandem solar cells, with efficiencies higher than the limit for single crystal silicon.
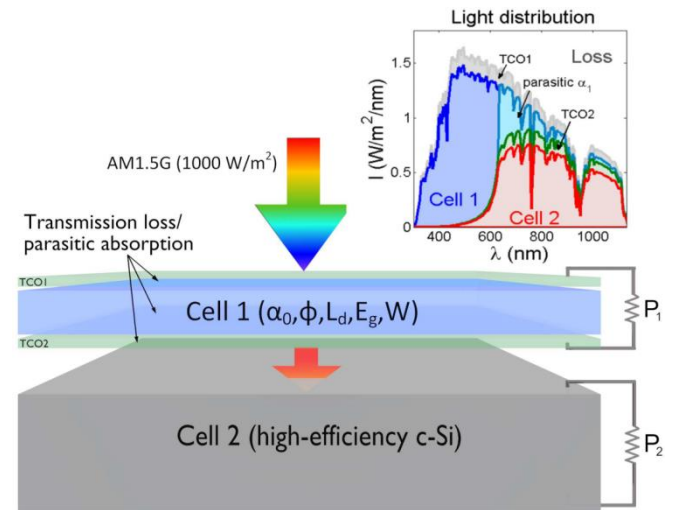

Figure 1 – Schematic representation of a four-terminal tandem cell on silicon. (Inset) Optical distribution of absorbed sunlight (AM1.5G) through the complete tandem structure. From [5], reproduced with permission from IEEE.

In order to reach the potential of perovskite/silicon tandems, it is important to consider optical losses very carefully (Fig. 1). A perovskite/Si tandem consists of a perovskite solar cell with a top transparent conducting oxide (TCO) layer, and either a rear transparent conducting layer (for a 4-terminal tandem) or a tunnel junction (for a 2-terminal tandem). Currently parasitic absorption in TCO layer is about 10% per layer. Together with reflectance losses, this means that we can expect loss of about 20% of sub-bandgap light with present technology. This leads to required top-cell efficiencies of 18% at a bandgap of 1.5eV just to break even and 23% to reach tandem efficiencies of 30% [2]. Reduction of these losses would increase the efficiencies that are achievable, making the technology more attractive for commercialization.

Current challenges for the optical engineering of single junction silicon cells are reflection control and incomplete light absorption due to non-ideal light trapping. Theoretically, isotropic Lambertian light trapping can increase the current density for a $100\mu m$ thick Si solar cell from about $38mA/cm^2$ to $43mA/cm^2$. Light trapping can also increase V_{oc}, by increasing the internal intensity of light. However, improvements in randomization of light and surface passivation are necessary before these improvements can be fully realized. One promising approach for extremely low reflectance is 'black silicon', produced by reactive ion etching or femtosecond laser texturing. Achieving low reflectance together with low recombination is generally a challenge, though recently effective surface recombination velocities of less than 10cm/s and 1% solar weighted reflectance have been reported [3].

A further challenge is integration of novel structures into high efficiency cells, as cell fabrication has many interdependent processes, and it is necessary that they be optimized simultaneously.

Advances in Science and Technology to Meet Challenges – There are several major areas where advances in optics are important in order to improve silicon cells and silicon/perovskite tandems.

The first is the development of low loss transparent conductors. Candidate materials for reducing the loss are graphene and nanophotonic structures [see section 8]. There has been some work done here with silver nanowires [4], but there is a great deal of scope for improvement using controlled designs and different materials.

For perovskite tandems, wavelength-selective light trapping may provide a route to high efficiency, as tandem efficiencies greater than 30% are potentially possible with diffusion lengths less than 100 nm. At an optimal top-cell bandgap of 1.7 eV, with diffusion lengths of current $CH_3NH_3PbI_xCl_{1-x}$ perovskites, tandem efficiencies beyond 35% are potentially achievable, but this will require low loss TCOs and highly effective wavelength selective light trapping [5].

A third major area for improvement is light trapping for silicon cells. It is incomplete light trapping and reflection, rather than parasitic loss, that are limiting current in silicon solar cells. Fig. 2 shows some of the structures that have been used to provide light trapping and reflection control in silicon solar cells. Metal nanoparticles in combination with a diffuse reflector can give comparable light trapping to pyramids [6]. Both pyramids and plasmonic particles give light trapping that is compatible with currents of over 42 mA/cm^2, but there is still scope for an extra 1 mA/cm^2. Even with plasmonic particles, improving light trapping is more important than reducing loss [see sections 9,13].

It is also worth pointing out what we don't need for these particular applications. For example, there has been quite a bit of work on exceeding the Lambertian limit for light trapping. However, this is only of interest for very thin structures [see section 8]. For a 100 μm or thicker silicon solar cell, and for perovskite solar cells, there is no significant benefit in above Lambertian light trapping.

Concluding Remarks – The global photovoltaic market is worth about $100 billion, and is completely dominated by silicon. The challenge here for optics is to use our greatly improved ability to understand and engineer optical structures at the nanoscale to improve the efficiencies of silicon-based solar cells to levels never before seen. There are important near-term and longer trajectory opportunities for both standard silicon cells and the rapidly emerging silicon-based tandems as solar continues to play an ever-increasing role in our energy future.
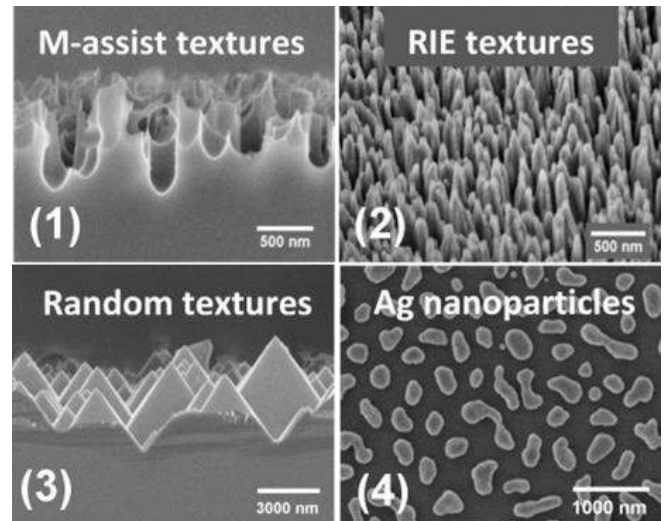

Figure 2 – SEM images of various types of texture structures on silicon: (1) metal-assisted etched texture (side view); (2) reactive ion etched texture (angle view); (3) random pyramid texture (side view) and (4) plasmonic Ag nanoparticles on silicon wafers (top view). Adapted from [6], with permission from the Optical Society of America.

References
[1] S. Mokkapati and K. R. Catchpole, "Nanophotonic light trapping in solar cells," *J. Appl. Phys.*, p. 101101, 2012.
[2] White et al., T.P, "Tandem Solar Cells Based on High-Efficiency c-Si Bottom Cells: Top Cell Requirements for >30% Efficiency," *IEEE J. Photovoltaics*, vol. 4, no. 1, p. 208, 2014.
[3] Allen et al., T, "Reactive Ion Etched Black Silicon Texturing: A Comparative Study," in *IEEE Photovoltaic Specialists Conference*, Denver, 2014.
[4] S. De et al., "Silver Nanowire Networks as Flexible, Transparent, Conducting Films: Extremely High DC to Optical Conductivity Ratios," *ACS Nano*, vol. 3, no. 7, p. 1767, 2009.
[5] Lal et al., N, "Optics and Light Trapping for Tandem Solar Cells on Silicon," *IEEE J. Photovoltaics*, vol. 4, no. 6, p. 1380, 2014.
[6] Barugkin et al., C, "Light trapping efficiency comparison of Si solar cell textures using spectral photoluminescence," *Optics Express*, 2015.

4. Photon recycling versus luminescence extraction, for record photovoltaic efficiency

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Status – There has been great progress in solar cell efficiency by the recognition of the need for luminescent extraction from solar cells, which now reach 28.8% efficiency [1] in the flat-plate, single junctions. (This is to be compared [2] with the Shockley-Queisser [3] limit, 33.5% efficiency [see section 1].) The improvement is often mistakenly attributed to "photon recycling", but that is only a special case of the real mechanism, luminescence extraction, which can be present with or without photon recycling.

Challenges and Advances in Science and Technology – The idea that increasing light emission improves open-circuit voltage seems paradoxical, as it is tempting to equate light emission with loss. Basic thermodynamics dictates that materials that absorb sunlight must emit in proportion to their absorptivity. At open circuit, an ideal solar cell would in fact radiate out from the solar cell, a photon for every photon that was absorbed. Thus the external luminescence efficiency is a gauge of whether additional loss mechanisms are present. At the power-optimized operating bias point, the voltage is slightly reduced and 98% of the open-circuit photons are drawn out of the cell as real current. Good external extraction at open circuit comes at no penalty in current at the operating bias point.

On thermodynamic grounds, Ross derived [4] that the open circuit voltage is penalized by poor *external luminescence efficiency η_{ext}* as:

$$qV_{OC} = qV_{OC\ Ideal} \quad kT\left|\ln \quad_{ext}\right| \qquad (1)$$

where η_{ext} is the probability of an internally radiated photon eventually escaping from the front surface of the cell. Equation (1) can be derived through the detailed balance method [2] of Shockley and Queisser, (SQ). M. A. Green already inferred [5] the external luminescence yield, η_{ext}, of all the different historical solar cell materials, from their respective record {$V_{OC\text{-}ideal} - V_{OC}$}, employing Equation (1).

As solar efficiency begins to approach the SQ limit, the internal physics of a solar cell transforms. Shockley and Queisser showed that high solar efficiency is accompanied by a high concentration of carriers, and by strong fluorescent emission of photons. Photons that are emitted internally are likely to be trapped, re-absorbed, and re-emitted, i.e. "photon recycling", which can assist the external luminescent emission at open-circuit. Alternately, surface texture on the solar
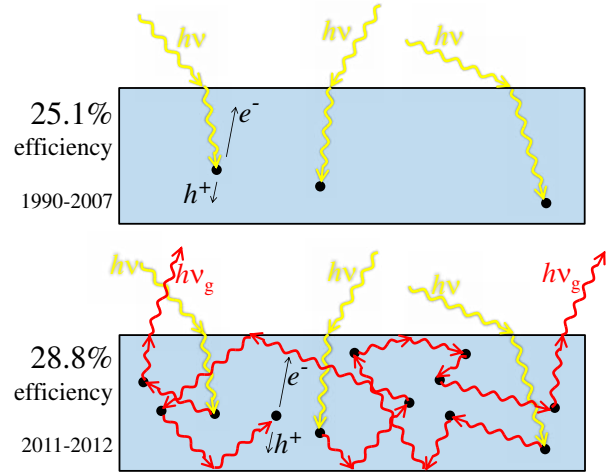

Figure 1 – The physical picture of high efficiency solar cells, compared to conventional cells. In high efficiency solar cells, good luminescent extraction is a requirement for the highest open circuit voltages. One-sun illumination is accompanied by up to 40-suns of trapped infrared luminescence, leading to the maximum external fluorescence efficiency. Reproduced from Ref [2] with permission of IEEE.

cell, often added for absorption enhancement, equally well lead to external luminescence extraction by random scattering, not requiring "photon recycling" at all. These two distinct mechanisms were first identified by Lundstrom [6].

The requirement for efficient luminescence extraction is accompanied by many suns of trapped internal luminescence in high index, high efficiency solar cells, >26% efficiency, as illustrated in Figure 1:

To resolve the paradox of why external luminescence is good for solar cell efficiency, there are a number of different explanations:

1. Good external luminescence is a gauge of few internal loss mechanisms. At open circuit, an ideal solar cell radiates a photon for every absorbed photon. When electron-hole pairs recombine non-radiatively or when photons are absorbed without generating photocarriers within the active part of the device, both the external luminescence efficiency and the cell efficiency decrease.

2. In a rate equation analysis, external emission of photons into free space is unavoidable. All other losses can, in principle, be eliminated. Thus the total losses are at their very least, when external emission is the only loss mechanism. Maximum external emission is minimum total losses, which leads to the highest efficiency.

3. In un-textured cells, good external luminescence requires recycled photons, and re-absorption. Internal reabsorption recreates the electron-hole pair, effectively extending the minority carrier lifetime. The

longer lifetime leads to a higher carrier density. Free energy, or voltage, increases with the logarithm of density.

4. The solar cell and the light-emitting-diode are equivalent, but reciprocal devices. Just as external emission leads to the most efficient light-emitting-diode, the reciprocal device also benefits when there are no other "loss" mechanisms.

5. External luminescence is sometimes used as a type of contactless voltmeter, indicating the separation of quasi-Fermi levels in the solar material. This is sometimes employed as a contactless, quality-control-metric, in solar cell manufacturing plants. In this viewpoint, it is tautological: Good external luminescence actually IS good voltage, and therefore good efficiency.

This is the preferred explanation for the paradox: *Good external luminescence IS good voltage.*

Concluding Remarks – Counter-intuitively, efficient external luminescence is a necessity for achieving the highest possible solar cell efficiency. Why would a solar cell, intended to absorb light, benefit from emitting light? Although it is tempting to equate light emission with loss, paradoxically, light emission actually improves the open-circuit voltage, and the efficiency. The voltage boost generally arises from luminescence extraction, for which photon recycling is only one possible mechanism.

References
[1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, & E. D. Dunlop, "Solar cell efficiency tables (version 39)," *Prog. Photovolt: Res. Appl.* 20, 2012, pp. 12-20, and earlier editions of solar cell records
[2] O.D. Miller, E. Yablonovitch, and S.R. Kurtz, "Intense internal and external fluorescence as solar cells approach the Shockley-Queisser efficiency limit", *J. Photovoltaics,* 2(3), pp. 303-311, http://arxiv.org/abs/1106.1603, http://dx.doi.org/10.1109/JPHOTOV.2012.2198434
[3] W. Shockley and H.J. Queisser, "Detailed balance limit of p-n junction solar cells," *J. Applied Physics* 32, 510, 1961
[4] R.T. Ross, "Some thermodynamics of photochemical systems," *J. Chem. Physics* 46, 1967, pp. 4590-4593
[5] M. A. Green, "Radiative efficiency of state-of-the-art photovoltaic cells," *Prog. Photovolt: Res. Appl.*, 20(4), pp. 472–476, 2012, doi: 10.1002/pip.1147
[6] G. Lush and M. Lundstrom, "Thin film approaches for high efficiency III-V cells", *Solar Cells* 30, 337 1991

5. Quantum-confined semiconductor nanostructures for enhanced solar energy photoconversion – Matthew C Beard

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Status – New PV technologies should have the potential to achieve power conversion efficiencies (PCE) beyond ~33% as well as reduce module costs. In 1982, Ross and Nozik determined that the PCE of unconcentrated solar irradiance into electrical or chemical free energy could be as high as ~66% for a single-junction solar converter when the excess kinetic energy of photogenerated electron-hole (e-h) pairs is harnessed without allowing it to dissipate as heat.[1] Excess energy arises from carriers that are generated with photon energies greater than that of the semiconductor band gap. Semiconductor nanostructures, where at least one dimension is small enough to produce quantum confinement effects, provide new pathways for energy management and have the potential to increase the efficiency of the primary photoconversion step so as to approach the Ross-Nozik limit [see sections 6, 8,9,13].

Multiple exciton generation (MEG), also called carrier multiplication, is a process where charge carriers with sufficient excess kinetic energy expend that energy via excitation of additional e-h pairs instead of dissipating the excess energy as heat. In bulk semiconductors, the latter process is limited by both momentum and energy conservation. In quantum-confined nanocrystals, or quantum dots (QDs), it is only limited by energy conservation. Thus, a MEG-active solar cell with nanocrystals could achieve a PCE of ~ 44% at one sun and ~ 85% under full concentration.[2]

In 2004, Schaller and Klimov developed a method of measuring the number of e-h pairs produced per absorbed photon in colloidal QD samples using ultrafast transient absorption spectroscopy.[3] The QD system of PbSe and PbS has received the most attention and is used to benchmark the prospects for quantum-confined nanostructures. The MEG process is enhanced by a factor of ~3 going from bulk PbSe to quasi-spherical PbSe nanocrystals (Fig. 1). Further enhancements have been observed with more complex nanostructures such as quantum rods (QRs),[4] quantum platelets (QPs)[5], and nanoheterostructures.[6]

Incorporating QDs into solar energy conversion architectures is an active area of research,[7] with current efforts now approaching a PCE of 10%. These approaches employ electronically coupled QDs in films, allowing for transport of electrons and holes within QD-layers to their respective electrodes. In 2011, Semonin et. al. fabricated a PbSe QD solar cell that achieved an external quantum efficiency
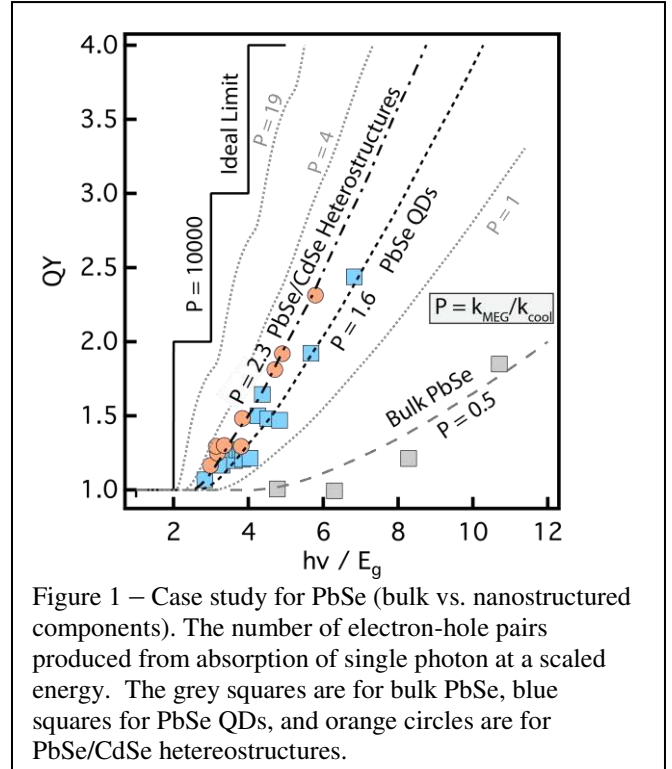

Figure 1 – Case study for PbSe (bulk vs. nanostructured components). The number of electron-hole pairs produced from absorption of single photon at a scaled energy. The grey squares are for bulk PbSe, blue squares for PbSe QDs, and orange circles are for PbSe/CdSe hetereostructures.

exceeding 100% for high energy photons.[8] This result demonstrated that QD-based solar cells have the potential to bypass the Shockley-Queisser limit and approach the Ross-Nozik limit.

Current and Future Challenges – When MEG is in competition with other exciton cooling mechanisms, the number of e-h pairs generated per absorbed photon (QY) can be expressed as,[9]
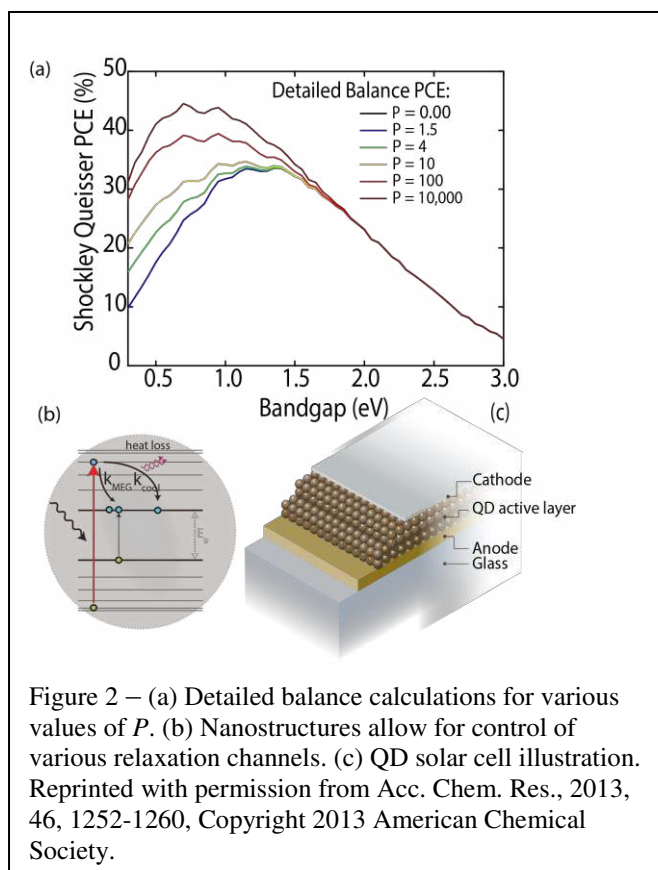
$$QY = 1 + \frac{k_{MEG}^{(1)}}{\left(k_{MEG}^{(1)} + k_{cool}\right)} + \frac{k_{MEG}^{(1)} k_{MEG}^{(2)}}{\left(k_{MEG}^{(1)} + k_{cool}\right)\left(k_{MEG}^{(2)} + k_{cool}\right)} + \dots$$

where $k_{MEG}^{(i)}$ is the rate of producing (i+1) excitons from (i) hot excitons and k_{cool} is the exciton cooling rate via heat generation. The ratio of k_{MEG} and k_{cool} can be characterized by a parameter, P (Fig. 1). P increases from ~ 0.5 for bulk PbSe to 1.6 for PbSe QDs and further increases to ~ 2.3 for nanoheterostructures[6] and QRs.[4]

In the case where only energy conservation limits MEG and P is large, two electron-hole pairs could be produced with photons whose energy is twice the semiconductor bandgap ($2E_g$), three at $3E_g$, 4 at $4E_g$, etc. (black staircase line in Fig. 1). In bulk PbSe the onset for producing multiple carriers per absorbed photon is ~ 6.3 E_g and to produce two e-h pairs requires ~ 11.5 E_g (Fig. 1, gray squares). The onset energy and the QY are related and can be combined to calculate an MEG efficiency. For bulk PbSe, the MEG efficiency is ~0.19. For PbSe QDs, the MEG efficiency increases to ~0.5, showing a decrease of the onset energy to ~3 E_g and production of 2 e-h pairs when the

photon energy reaches ~6 E_g (Fig. 1, blue squares). Future research should determine systems that can further approach the staircase characteristics.

The thermodynamic PCE limit of solar cells is a function of P (Fig. 2). For example, the PCE limit is ~44% when P is large and 39% with a P of 100. These conditions should be achievable within suitably designed quantum confined nanostructures. For example, recent efforts within Si nanostructures suggest that such high MEG efficiencies are achievable.[10]

Figure 2 − (a) Detailed balance calculations for various values of P. (b) Nanostructures allow for control of various relaxation channels. (c) QD solar cell illustration. Reprinted with permission from Acc. Chem. Res., 2013, 46, 1252-1260, Copyright 2013 American Chemical Society.

Advances in Science and Technology to Meet Challenges – Semiconductor nanocrystals offer many avenues towards increasing the MEG yields through internal and external modifications. To achieve the largest benefit, one should either look for systems that can reduce k_{cool} or increase k_{MEG}. Within the Fermi-golden rule approximation, k_{MEG} depends upon two factors: (1) the density of final biexciton states, $_f$; and (2) the Coulomb matrix element, W_c. To achieve improvements in these characteristics, researchers are exploring several options: (1) multicomponent systems where either the electron or hole experience slowed cooling that allows for a greater probability of undergoing MEG.[6] Multicomponent systems may also increase W_c by breaking the spherical symmetry and thereby decreasing carrier screening effects. Enhanced MEG in QRs and QPs can also be ascribed to such a

breaking of spherical symmetry. (2) New low bandgap semiconductor systems. A good place to start is those systems with known low electron-phonon coupling strengths[9] and/or are semi-metals in bulk form (such as HgTe, graphene, -Sn) but whose bandgap can be tuned via quantum-confinement effects. (3) Matrix-QD coupling effects that can achieve slowed cooling and/or higher W_c.[11]

In order to identify new systems with enhanced MEG characteristics, researchers should develop new faster and more robust means of testing for MEG as well as theory to predict promising systems for exploration. Currently, the most used approach for measuring carrier yields is based upon ultrafast transient absorption (TA) or photoluminescence (PL) spectroscopy.[3, 9] Both techniques are laborious and prone to experimental errors and thus great care must be taken in order to extract the photon-to-carrier quantum yield.[9] Solar cell architectures where current is measured are preferable.[8] Developing a QD solar cell from QD systems can be time consuming and thus knowing whether high MEG yields are possible prior to undertaking such an endeavor is necessary.

Developing device current-based approaches for measuring enhanced light to current yields but which are less complex than a solar cell should be pursued. For solar cells, the basic strategy is to sandwich a QD-layer between an *n*-type window layer, which accepts electrons while blocking holes, and a metal electrode that accepts holes. Light is absorbed in the QDs and excitons separate to form free electrons and holes. Critical issues that need to be addressed are robustness of QD-layer formation and optimization of the front and back interfaces. Adapting such architectures for fast and reliable MEG measurements would benefit the search for systems with enhanced MEG characteristics.

Concluding Remarks – Quantum dot solar cells remain a promising technology for inexpensive, scalable, and efficient solar cells. Such semiconductor nanostructures are synthesized in solution phase chemical reactions, where the reaction conditions can be modified to produce a variety of shapes, compositions, and structures. Thanks to their size- and surface-tunability and solution processing, it should be possible to find systems that enable inexpensive and high efficient devices from QD-based inks. Surpassing the SQ limit for a single-junction solar converter system is a scientific and technological challenge with significant benefit to society. The challenge is to increase the MEG efficiency to approach the energy conservation limit.

References

[1] Ross, R. T.; Nozik, A. J., Efficiency of Hot-Carrier Solar Energy Converters. *J. Appl. Phys.* **1982,** *53*, 3813.

[2] Hanna, M. C.; Beard, M. C.; Nozik, A. J., Effect of Solar Concentration on the Thermodynamic Power Conversion Efficiency of Quantum-Dot Solar Cells Exhibiting Multiple Exciton Generation. *J. Phys. Chem. Lett.* **2012,** *3*, 2857-2862.

[3] Schaller, R.; Klimov, V., High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion. *Phys. Rev. Lett.* **2004,** *92*, 186601.

[4] Padilha, L. A.; Stewart, J. T.; Sandberg, R. L.; Bae, W. K.; Koh, W. K.; Pietryga, J. M.; Klimov, V. I., Aspect Ratio Dependence of Auger Recombination and Carrier Multiplication in PbSe Nanorods. *Nano Lett.* **2013,** *13*, 1092-1099.

[5] Aerts, M.; Bielewicz, T.; Klinke, C.; Grozema, F. C.; Houtepen, A. J.; Schins, J. M.; Siebbeles, L. D. A., Highly efficient carrier multiplication in PbS nanosheets. *Nat Commun* **2014,** *5*.

[6] Cirloganu, C. M.; Padilha, L. A.; Lin, Q.; Makarov, N. S.; Velizhanin, K. A.; Luo, H.; Robel, I.; Pietryga, J. M.; Klimov, V. I., Enhanced carrier multiplication in engineered quasi-type-II quantum dots. *Nat Commun* **2014,** *5*, 4148.

[7] Kramer, I. J.; Sargent, E. H., The Architecture of Colloidal Quantum Dot Solar Cells: Materials to Devices. *Chem. Rev.* **2014,** *114*, 863-882.

[8] Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H. Y.; Gao, J. B.; Nozik, A. J.; Beard, M. C., Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011,** *334*, 1530-1533.

[9] Beard, M. C.; Luther, J. M.; Semonin, O. E.; Nozik, A. J., Third Generation Photovoltaics based on Multiple Exciton Generation in Quantum Confined Semiconductors. *Accounts of Chemical Research* **2013,** *doi: 10.1021/ar3001958*.

[10] Timmerman, D.; Valenta, J.; Dohnalova, K.; de Boer, W.; Gregorkiewicz, T., Step-like enhancement of luminescence quantum yield of silicon nanocrystals. *Nature Nanotechnology* **2011,** *6*, 710-713.

[11] ten Cate, S.; Sandeep, C. S. S.; Liu, Y.; Law, M.; Kinge, S.; Houtepen, A. J.; Schins, J. M.; Siebbeles, L. D. A., Generating Free Charges by Carrier Multiplication in Quantum Dots for Highly Efficient Photovoltaics. *Accounts of Chemical Research* **2015,** *48*, 174-181.

6. Challenges and advances in fabrication of quantum dot intermediate band solar cells –

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Status – The quantum dot intermediate band solar cells (QD-IBSCs) which commonly suffer from small absorption and low density of QDs, result in a drop of V_{OC}. However, V_{OC}, and hence the efficiency, recovers fast and cell performance improves with concentrated illumination of sunlight [1]. Current QD-IBSCs require light concentration to ensure that the photo-generation rate outperforms the recombination rate *via* IB states. The areal density of QDs has direct influence on the generation and recombination processes *via* IB because the density of states of IB (N_{IB}) is linked to the areal density as, $N_{IB} = N_{areal} \times N_{stacks} / W$, where N_{areal} is the areal density of QDs array, W is the intrinsic QD region width, and N_{stacks} is the number of QD stacks.

Assuming an energy bandgap of $E_g = 1.40$eV for GaAs host material, the generation and recombination rates for the widely-studied InAs/GaAs QD-IBSC with different positions of IB can be calculated based on the detailed balance theory as shown in Fig. 1 [2]. Here the QDs areal density corresponds to the total QDs density given by $N_{areal} \times N_{stacks}$. The absorption cross sections are taken as 3×10^{-14} cm^2 for both optical transitions between VB to IB and IB to CB. It can be clearly seen that if the QD areal density is below 1×10^{16} cm^{-2}, the net generation rate G_{net} becomes *negative* with deepening the location of IB in the QD region.

The highest areal density of InAs QDs on GaAs experimentally demonstrated to date is ~ 1×10^{12} cm^{-2} [3], which means that the recombination rate would dominate over the photo-generation rate under 1 sun as from Fig. 1. However, the situation will significantly improve if the cell is under light concentration. Figure 2 shows the dependence of net generation rate G_{net} on concentration ratio for the case of IB being located at 0.2 eV below the CB edge. It shows that G_{net} turns into *positive* after 10 suns. When the concentration exceeds 1000 suns, a positive G_{net} value can be expected even for the QDs areal density of 1×10^{12} cm^{-2}, and the simulation results are consistent with the experimental results reported in literature [4,5].

Current and Future Challenges – In the last decade, there has been an extensive effort to demonstrate QD-IBSCs with high-efficiency. The QDs are required to be homogeneous and small in size and to be regularly and tightly positioned in the active region of the cell, in order to form of an IB or a superlattice miniband that is well separated in energy from the higher energy states [6]. Further, dense QDs arrays are required to achieve sufficient photo-absorption resulting in a positive G_{net}. The most commonly used fabrication method of QDs structure is to utilize spontaneous self-assembly of coherent 3-dimensional (3D) islands in lattice-mismatched heteroepitaxy, the Stranski-Krastanov (S-K) growth mode in MBE or MOVPE. The InAs/GaAs material system has a lattice mismatch of 7.2%, and the strain induced by this lattice mismatch drives into 3D coherent S-K growth after formation of a thin 2D InAs wetting layer in the initial growth stage. The typical areal density of InAs QDs achieved by S-K mode is $N_{areal} = 10^{10} \sim 10^{11}$ cm^{-2} grown on GaAs (001) substrate. However, the size is still large and density is much less than what is required. The QDs size and density are dependent on the growth conditions such as the V/III flux ratio, substrate orientation, growth
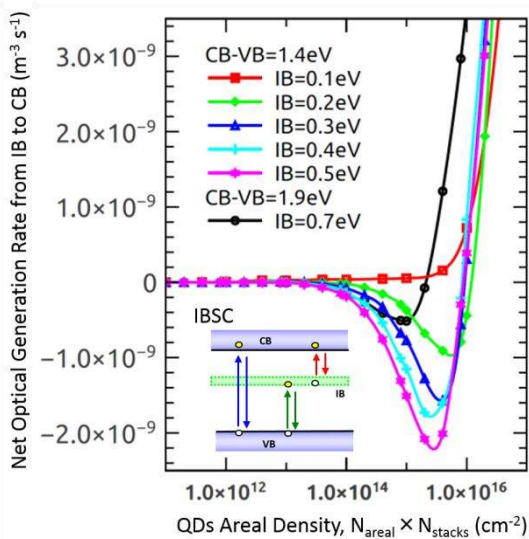

Figure 1 – Detailed balance calculation of the dependence of net generation rate from IB to CB, G_{net} on InAs QDs density and IB energy position relative to CB bandedge. Reproduced with permission from [2].
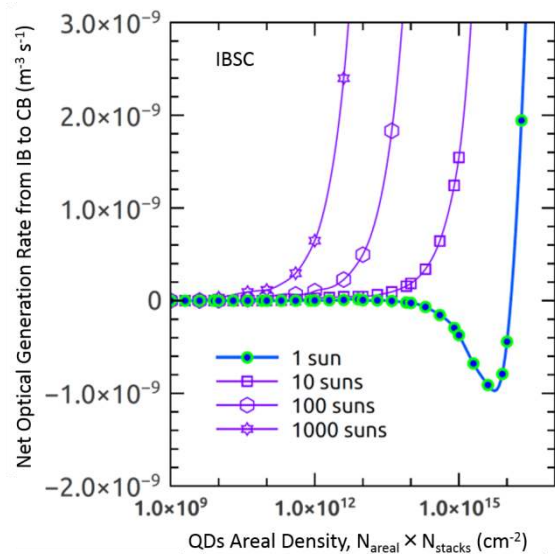

Figure 2 – Detailed balance calculation of the dependence of G_{net} on concentration ratio. The IB is located at 0.2 eV below the CB edge. Reproduced with permission from [2].

temperature, and material used for the buffer layer. The areal density of QDs is increased by irradiating Sb to the buffer or wetting layer and Yamaguchi *et al*. have recently demonstrated $N_{areal} = 1 \times 10^{12}$ cm^{-2} [3].

For further increasing of total QDs density, the fabrication of multi-stacking configuration is necessary. One has to consider that a gradual build-up of internal lattice strain with increased number of stacking leads to an increase in both the size and its fluctuation for the multi-stacked QDs grown by S-K growth. In addition, the strain accumulated above the critical thickness generally results in a generation of misfit dislocations, which occurs typically after 15-20 layers of stacking in the case of InAs/GaAs QDs growth. Recently, Sugaya *et al*. have demonstrated stacking of In$_{0.4}$Ga$_{0.6}$As/GaAs QDs fabricated by intermittent deposition technique [7]. The critical thickness of In$_{0.4}$Ga$_{0.6}$As/GaAs system is much thicker than that of InAs/GaAs system, and no dislocations are generated even after stacking up to 400 In$_{0.4}$Ga$_{0.6}$As QD layers.

Meanwhile, tensile-strained barriers have been studied in order to compensate for the compressive strain induced by the QDs layers. This growth method is called the strain-compensation or strain-balanced technique, and to date, InAs QDs in AlGaInAs matrix on InP substrate, InAs QDs in GaAsP, and in GaP matrix on GaAs substrate, and InAs QDs in GaNAs on GaAs (001), and on (311)B substrate of high material quality have been reported [8].

Advances in Science and Technology to Meet Challenges – The IBSC concept shown in the inset of Fig. 1 represents the optimal cell configuration under maximum solar concentration. However, practical solar cells operate at lower solar concentrations, usually below ~1000 suns, and there is an efficiency advantage to be gained by introducing a relaxation stage. The principle is that the optical transitions between this relaxed IB, or so called a ratchet band (RB) and VB are critically forbidden, hence the only route for relaxation *via* the IB now involves surmounting a potential barrier from the RB to VB. The fundamental efficiency benefit of relaxation has also been recognized in up-converting systems that rely upon sequential absorption. To date, a molecular system [9] and a ferromagnetic dilute magnetic semiconductor (DMS) [10] promoting this scheme have been proposed.

The electron lifetime in IB also directly influences the conversion efficiency of QD-IBSCs. The detailed balance calculations for the case of ideal IBSCs often neglect the effect of nonradiative lifetime. However, QDs have a finite nonradiative lifetime and could affect the photo-generation rate because they act as recombination centers just as absorption levels. The electron lifetime and hence the efficiency is influenced by the carrier recombination strength, and thermal escape, and tunneling escape rates out of QDs. A long electron lifetime is obtained by controlling the recombination rate using a type-II QD heterostructure, using a high potential barrier preventing the thermal carrier escape from QDs, and by introducing an electric field damping layer preventing the field-assisted tunneling out of QDs. Further, introducing a RB into the solar cell assists with the problem of maintaining long carrier lifetime. Assuming that the VB-IB transition is direct and allowed, a typical electron lifetime in IB of the order of 10 ns can be assumed. Assuming a Boltzmann statistics for the electron distribution, introducing the relaxation step of ΔE (between IB and RB) could increase the lifetime by a factor exp ($\Delta E = k_B T$). This effect is responsible for intermediate state lifetimes of order 100 μs measured in some molecular up-conversion systems.

Concluding Remarks – Significant efforts and a rapid progress have been made in the device physics as well as practical demonstration of high-efficiency IBSCs. These achievements have been possible due to mature and highly uniform III-V QDs and nanostructure material growth and processing technology. For this, the demonstration of QDs-based IBSCs is presently undergoing three main stages. The first is to develop technology to fabricate high-density QDs arrays or superlattice of low defect density and long electron lifetimes. The strain-compensated or strain-balanced growth technique significantly improves the QDs material quality and characteristics of SCs even after stacking of 100 QDs layers or more in S-K growth. The second is to increase the carrier lifetime in IB states by controlling the recombination rate using a type-II QD heterostructure, a high potential barrier preventing the thermal carrier escape from QDs, and an electric field damping layer preventing the field-assisted carrier escape. Further, introducing a RB into the solar cell assists with the problem of maintaining long carrier lifetime. The last is to realize ideally half-filled IB states to maximize photocurrent generation by two-step photon absorption. The doping of IB region, photofilling by light concentration, and photon confinement structures are all considered important.

In addition to further improvements in the material quality, the control of absorption matching in IB materials are expected to improve the efficiency of QD-IBSCs in the near future [see also sections 5,14].

References
[1] A. Luque, A. Marti, and C. Stanley, Nat. Photonics **6**, 146 (2012).
[2] Y. Okada, N. J. Ekins-Daukes, T. Kita, R. Tamaki, M. Yoshida, A. Pusch, O. Hess, C. C. Phillips, D. J.

Farrell, K. Yoshida, N. Ahsan, Y. Shoji, T. Sogabe, and J.-F. Guillemoles, Appl. Phys. Rev. **2**, 021302 (2015).

[3] K. Sakamoto, Y. Kondo, K. Uchida, and K. Yamaguchi, J. Appl. Phys.**112**, 124515 (2012).

[4] V. M. Lantratov, S. A. Mintairov, S. A. Blokhin, N. A. Kalyuzhnyy, N. N. Ledentsov, M. V. Maximov, A. M. Nadtochiy, A. S. Pauysov, A. V. Sakharov, and M. Z. Shvarts, Adv. Sci. Technol. **74**, 231 (2010).

[5] T. Sogabe, Y. Shoji, M. Ohba, K. Yoshida, R. Tamaki, H.-F. Hong, C.-H. Wu, C.-T. Kuo, S. Tomić, and Y. Okada, Sci. Rep. **4**, 4792 (2014).

[6] S. Tomić, T. S. Jones, and N. M. Harrison, Appl. Phys. Lett. **93**, 263105 (2008).

[7] T. Sugaya, T. Amano, M. Mori, S. Niki, and M. Kondo, Jpn. J. Appl. Phys., Part 1 **49**, 030211 (2010).

[8] Y. Okada, K. Yoshida, Y. Shoji, and T. Sogabe, IEICE Electron. Express **10**, 20132007 (2013).

[9] N. J. Ekins-Daukes and T. W. Schmidt, Appl. Phys. Lett. **93**, 063507 (2008).

[10] P. Olsson, C. Domain, and J.-F. Guillemoles, Phys. Rev. Lett. **102**, 227204 (2009).

7. Advanced materials for solar energy conversion

– Stephan Lany[1], Talia Gershon[2] and Andriy Zakutayev[1]
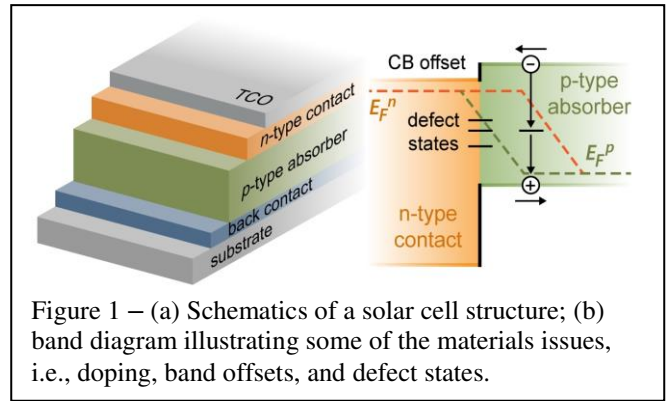
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Status – The photovoltaic (PV) market, dominated by c-Si technologies, has seen remarkable cost reductions in recent years The current module cost of 0.5-0.7 \$/W should translate into 5-10 c/kWh electricity prices after further reductions in the balance of system and soft costs. However, recent macroeconomic analysis [1] suggests that the scaling to and beyond the terawatt (TW) level will depend strongly on the rate of future capital investment in manufacturing capacities [see section 2]. Potential barriers towards multi-TW-scale PV include the relatively large capital expenditures (capex) for PV grade Si production, as well as supply limitations of Te and In for CdTe and $Cu(In,Ga)Se_2$ beyond the TW scale. The scalability challenge becomes an even bigger one if aiming for both electricity and fuel generation by solar energy conversion.

The development of new PV technologies based on novel advanced materials could create a new industry with independent supply chains, foster market diversification, and attenuate market volatility, and thereby enhance the odds for beyond-TW scaling of solar energy production [see also section 8]. Such *disruptive* PV technologies must be competitive with current technologies in efficiency, cost, and reliability, they must use readily available elements [2], but they also have to be compatible with low-capex production processes to ensure rapid industry growth after initial commercialization.

Over the past decade, considerable research efforts have addressed alternative approaches, including dye sensitized cells, and organic and inorganic PV. Particular noteworthy are the $Cu_2ZnSn(S,Se)_4$ kesterites [3], as well as the hybrid methyl-ammonium lead-halide perovskites ($MAPbI_3$) that have reached solar cell efficiencies above 20% in just a few years of research and development [4]. We note, however, that both systems must still overcome significant hurdles (e.g. performance, stability) before they will become commercial. Beyond the further development of such individual materials systems, the Materials Genome Initiative provides a framework for broader search, design, and discovery of materials for photovoltaics, solar fuel generation, and a wide range of other applications [5].

Current and Future Challenges – In order to identify promising and under-explored PV materials worthy of future development, the band gap and the optical absorption strength are often used as a first selection

Figure 1 – (a) Schematics of a solar cell structure; (b) band diagram illustrating some of the materials issues, i.e., doping, band offsets, and defect states.

criterion [2]. Despite being good screening metrics to quickly winnow out unfeasible candidates, there are many additional materials criteria needed to be fulfilled beyond the band gap and optical properties. The absorber material must have high carrier mobilities, particularly for minority carriers, low densities of detrimental point or extended defects (e.g., grain boundaries) that can accelerate recombination and limit minority carrier lifetimes, as well as a high level of control of the electrical doping to enable formation of *p-n* junction with a suitable depletion width.

Besides Si and epitaxial III-V systems, there are few known bipolar dopable semiconductors that could be suitable for *p-n* homo-junction PV. Therefore, most thin-film solar cells use a hetero-junction with two different materials (see Fig. 1): typically a *p*-type absorber and an *n*-type contact. In this configuration, the quality of absorber/contact hetero-interface becomes crucial for achieving high-efficiency cells, i.e., it should have low interface defect densities and a small conduction band offset. Considering that the interface at the back contact can also play a role in device performance, it is clear that the development of a new PV technology must address the entire device structure, not just individual absorber and contact materials.

A significant number of potential inorganic absorber materials have been suggested and studied in recent years, including Zn_3P_2, Cu_2SnS_3, WSe_2, Cu_2S, $ZnSnN_2$, FeS_2, $BiFeO_3$, Cu_2O, SnS, and Sb_2Se_3. However, solving all of the above-mentioned bulk transport and interface issues under the constraints of a limited choice of elements (availability, cost, toxicity), processing considerations, and anticipated production cost, remains a huge challenge. In particular, this task requires a balance between sufficient breadth and depth; we must address all requirements on the materials' bulk- and interface properties while at the same time screening a large number of materials including unconventional and unsuspected candidates that might have been overlooked before. Furthermore, the search should not only enumerate the possible stoichiometric binary, ternary, and multinary

compounds, but also include the possibility to design desirable properties through deliberate variation of the composition, such as in the case of semiconductor alloys. Considering the vastness of the full phase space of compositions and process parameters, it is clear that the traditional way of case-by-case studies is too time consuming. Thus, new research approaches (outlined below), and arguably also new funding mechanisms are needed to bridge the wide gap between basic materials science and the commercialization of new, TW-scalable PV technologies.

Advances in Science and Technology to Meet Challenges – In order to be successful, the research has to span the entire PV development cycle: from broad materials exploration, to targeted research on individual materials, to device integration and testing. This formidable task can be accomplished by the complementary use of computational materials science and synthesis / characterization / analysis. Besides accelerating the development cycle of investigations via high-throughput and combinatorial approaches for both computations and experiments, the research strategy should also include in-depth studies of the underlying materials science to distill composition-structure-property relationships and to formulate design rules. For example, the need for low-cost synthesis routes increases the need for "defect tolerant" materials, i.e., materials that maintain favorable electronic properties despite the presence of structural defects, disorder, or impurities [6].

Computational advances: High-throughput computing has enabled the creation of databases for structural, mechanical, thermodynamic, magnetic, and electronic properties [7]. The capability of GW quasi-particle energy calculations is now implemented in several electronic structure codes. Although limitations and challenges remain, particularly for more complex systems, the reliable GW prediction of band gaps and optical properties is now in reach for a broad range of materials. Supercell calculations, which are traditionally employed to describe doping and defects in the dilute limit, can now be extended to the case of aliovalent alloys, allowing the prediction of both band-gaps and doping as a function of composition [8], as illustrated in Fig. 2a for the case of Cu_2O-based alloy absorbers.

Experimental advances: Combinatorial experiments have traditionally been used to screen large elemental composition variations for their intrinsic properties such as crystal structure and absorption spectra. Recent advances in the combinatorial methods allow the deposition and analysis of "libraries" with a gradient in both composition and growth temperature, thereby enabling a high-throughput exploration of the phase space (see Fig. 2b as example for ZnO:Ga contact [9]).
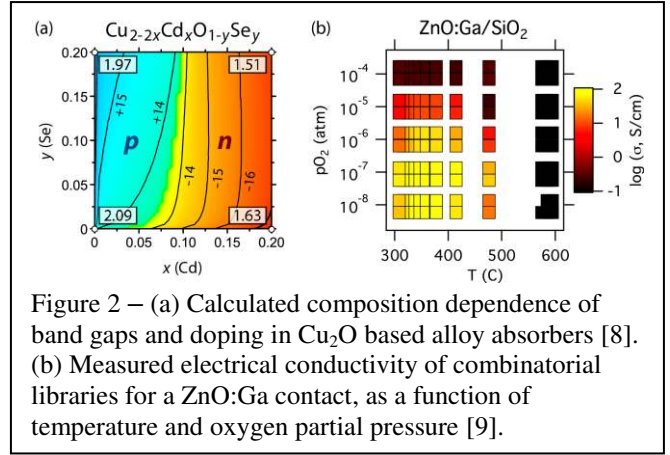

Figure 2 – (a) Calculated composition dependence of band gaps and doping in Cu_2O based alloy absorbers [8]. (b) Measured electrical conductivity of combinatorial libraries for a ZnO:Ga contact, as a function of temperature and oxygen partial pressure [9].

Finally, combinatorial optimization of multilayer PV devices is now possible [10], implicitly taking into account the interaction effects of individual materials layers at their interfaces, including band offsets, and inter-diffusion.

Future needs: Further development of computational capabilities would be desirable for the routine calculations of electron and hole mobilities and minority carrier lifetimes, which would enable device modeling based on computational parameters. In order to assess the electronic properties of the interface at hetero-junctions, it would be of high importance to establish theoretical methods for generating structural models of non-epitaxial interfaces. Development of faster and more accurate experimental methods for measuring the lifetimes of the photo-excited charge carriers and for determining band offsets at heterointerfaces is equally important. An additional research need is the improved understanding of non-equilibrium effects in thin-film deposition and the implications on the defect densities.

Concluding Remarks – Many promising photovoltaic materials remain undiscovered or underexplored due to lack information regarding their optoelectronic, structural, and intrinsic defect properties. Individual experiments exploring one composition at a time could consume years of effort before the system is fully understood. Reducing this time is therefore of paramount importance. Improvements in computational and experimental techniques are accelerating the screening of the fundamental optoelectronic and defect tolerance characteristics at the individual material level. This information is invaluable for down-selecting systems worthy of a more targeted development. Future approaches for developing new PV technologies will consider more specifically kinetic limitations during deposition and the structure and electronic properties of interfaces, which are crucially important for integrating individual materials into high-efficiency devices. The feedback between computational and experimental approaches will significantly reduce the time needed to achieve

disruptive materials discovery for TW-level PV production in the future.

References

[1] P.A. Basore, D. Chug, and T. Buonassisi, *Economics of future growth in photovoltaics manufacturing*, Proc. 42nd IEEE PV specialists conference (2015).

[2] C. Wadia, A.P. Alivisatos, and D.M. *Kammen, Materials availability expands the opportunity for large-scale photovoltaics deployment*, Environ. Sci. Technol. **43**, 2072 (2009).

[3] S. Siebentritt and S. Schorr, *Kesterites - a challenging material for solar cells*, Prog. Photovolt: Res. Appl. 20, 512 (2012).

[4] M.A. Green, A. Ho-Baillie, and H.J. Snaith, *The emergence of perovskite solar cells*, Nature Photonics **8**, 506 (2014).

[5] Materials Genome Initiative Strategic Plan (December 2014); https://www.whitehouse.gov/mgi

[6] A. Zakutayev, C.M. Caskey, A.N. Fioretti, D.S. Ginley, J. Vidal, V. Stevanovic, E. Tea, and S. Lany, *Defect tolerant semiconductors for solar energy conversion*, J. Phys. Chem. Lett. **5**, 1117 (2014).

[7] https://www.materialsproject.org; http://aflowlib.org; http://materials.nrel.gov

[8] V. Stevanovic, A. Zakutayev, S. Lany, *Composition dependence of the band gap and doping in Cu_2O-based alloys as predicted by an extension of the dilute-defect model*, Phys. Rev. Appl. **2**, 044005 (2014).

[9] A. Zakutayev, N. H. Perry, T. O. Mason, D. S. Ginley, and S. Lany *Non-equilibrium origin of high electrical conductivity in gallium zinc oxide thin films* Appl. Phys. Lett. **103**, 232106 (2013)

[10] S. Rühle, A. Y. Anderson, H.-N. Barad, B. Kupfer, Y. Bouhadana, E. Rosh-Hodesh, and A. Zaban, *All-Oxide Photovoltaics*, K. Phys. Chem. Lett., 3, 3755 (2012)

8. Going thin: atomic-layered 2D materials for photon conversion

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Status – The field of atomically thin 2-dimensional (2D) materials has grown rapidly over the last few years since it exhibits non-classical phenomena. The well-studied carbon material, graphene, is characterized by an absence of a band gap (for monolayers) [1]. This is relevant for photon absorption since unlike semiconductor materials this band structure is spectrally not band-edge limited, thus enabling broadband absorption. Transition-Metal-Dichalcogenides (TMD), however, do have a bandgap, and have been found to be stress and composition-bandgap tunable [2]. The bandgap (0.8 eV) of black phosphorous matches that of the telecom c-band (1550 nm), and hence could find applications in photo-receivers [3].

Taking a closer look at one materials system (MoS_2) reveals some unexpected properties relating to interactions with light; the band structure of MoS_2 transforms from being an indirect band gap (1.2 eV) for bulk material to a direct band gap (1.8 eV) for single-layers, which is accompanied by a 10^4-fold photoluminescence (PL) enhancement [2]. Unlike in classical physics where the optimum thickness of an absorber is given by the imaginary part of the permittivity, 2D materials behave quite differently. For instance, the photo-detection can be tuned for different wavelengths, where single- and double-layer MoS_2 absorbs green light, while triple-layer, which is less than a nanometer thicker absorbs in the red visible spectrum [4]. Such thickness-modulated absorption in conjunction with their relative earth abundance open up prospects for atom-thin 2D material-based multi junction solar cells that capture photons from the visible to the near-infrared.

Heterostructures such as MoS_2/graphene, or MoS_2/WS_2 have shown that a layer as thin as 1 nm are able to absorb 5–10% of the incident light [5]. This is an order of magnitude higher compared to the same thickness of GaAs or Si, and might translate into 1–3 orders of magnitude higher power densities than the best existing ultrathin solar cells. The origin for this is found in the electronic density of states (DOS), which exhibits peaks known as Van Hove singularities.

With intriguing prospects for 2D material-based for photon conversion applications, a variety of fundamental challenges need to overcome and investigated as discussed next.

Current and Future Challenges – For instance these atom-thin materials are rather sensitive to surface charges, neighboring materials, and stresses. While such sensitivity can be exploited (if properly controlled) to achieve higher functionality, the field is still in the exploratory phase. Improvements are needed from fundamental band structure engineering to control of chemical synthesis and material processing.

Although semiconducting TMDs exhibit high absorption coefficients, TMD-based PV cells with superior PV performance have yet to be demonstrated. This is because a monolayer material has obvious physical thickness limitations and is mostly transparent at visible frequencies. Furthermore, in order to obtain a reasonable photo current and voltage for PV applications, stacked multilayer devices might be needed. This however demands a clear understanding and control of the interface physics, and might encompass novel structures to increase the light-matter interaction, or processing approaches to create built-in potential in multilayers such as via plasma doping.

An exciting avenue for 2D materials is the controlled introduction of strain, which offers the flexibility in controllable and potentially tunable functionality for device engineering; strain reduces the crystal symmetry, leading to significant shifts in the energy band edges, which changes the electronic and optical properties of the material.

Regarding electron transport and FET devices, monolayer TMDs have shown low electronic mobility. For instance the value for single layer MoS_2 is about two orders of magnitude lower compared that of bulk. In this regard, a complete understanding of the microscopic picture for the electron transport in monolayer or few-layer TMD films remains unclear.

Regarding the synthesis of TMD sheets, low-temperature approaches and catalyst-free synthesis are highly desirable for practical applications. However, to date, no practical method for the large-scale, defect-free, and scalable production of TMD sheets with fine control over the number and the structure of the layers over the entire substrate has been developed. If successful, however, it would dramatically accelerate the production and deployment of these materials in photon conversion industries such as for PV. However, even if the synthesis is mastered, techniques for transferring large-scale TMD sheets also needs to be developed since direct-growth often conflicts with temperature budgets.

Advances in Science and Technology to Meet Challenges – Addressing the low photon absorption of 2D materials can be met by deploying light-matter interaction enhancement techniques. Here three options are possible; a) enhancing the optical DOS via incorporating optical cavities, b) designing momentum-bending options that feed waveguide-like

structures that allow for lateral (vs. normal) absorption, and c) field density enhancements using metal-optics approaches such as found in plasmonics, if loss management can be achieved.

Furthermore, physical strain creates an opportunity to create multi-bandgap designs within one material system. For instance, the induction of periodic changes in strain values could lead to advanced PV cells. Regarding the electrical transport, Lee et al [6] reported that although Van der Waals heterojunctions exhibits both rectifying electrical characteristics and photovoltaic response, the underlying microscopic processes differ strongly from those found in conventional devices in which an extended depletion region play a crucial role. In atomic heterostructures the tunneling-assisted interlayer recombination of the majority carriers is responsible for the tunability of the electronic and optoelectronic processes.

Interestingly, the combination of multiple 2D materials has been shown to provide high photon conversion performance; for instance sandwiching an atomic p–n junction between graphene layers enhances the collection of the photoexcited carriers [6]. Hexagonal boron nitride (h-BN) was shown to be a promising substrate (improved 2D material mobility) for high-quality 2-D electronics due to its atomically smooth surface that is relatively free of dangling bonds and charge traps [7].

On the processing side, plasma-assisted doping can serve as a reliable approach to form stable p-n junctions in multilayer MoS_2 resulting in a significant enhancement of the photovoltaic response such as higher open circuit voltage and a lower dark current [8]. Applying field enhancement techniques via using plasmonic resonances in nanoparticles can improve absorption; Britnell et al. placed Gold nanospheres on top of the 2D heterostructures showing a 10-fold the photocurrent to increase [9]. Rolling a stacked hetero-layer of semiconducting, metallic, and insulating 2D materials in a core-shell fashion allows for broadband photo-absorption up to 90% due to a broadband nano-cavity, and an opportunity for strain-engineering for multi band gap PV cells [10].

Concluding Remarks – Although still at an early stage of development, the known properties of atomically thin material systems for photon conversion are motivating for on-going research. Together with graphene and insulating materials such as h-BN, 2D semiconducting materials are an attractive choice for constructing solar cells on flexible and transparent substrates with ultra-thin form factors, and potentially even for mid-to-high efficiency solar cells. While some fundamental and practical challenges are still present, the field of nanophotonics has a wide variety of

toolkits available towards handling these challenges. In addition, 2D materials show a decent potential for highly functional and tunable material platforms, if synthesized and controlled properly. Incidentally, the latter is the aim of the Materials Genome Initiative and the DMREF program of the National Science Foundation of the U.S. [see also section 7]. In conclusion, the rapid progress of this field might overcome control and design challenges in the near future.
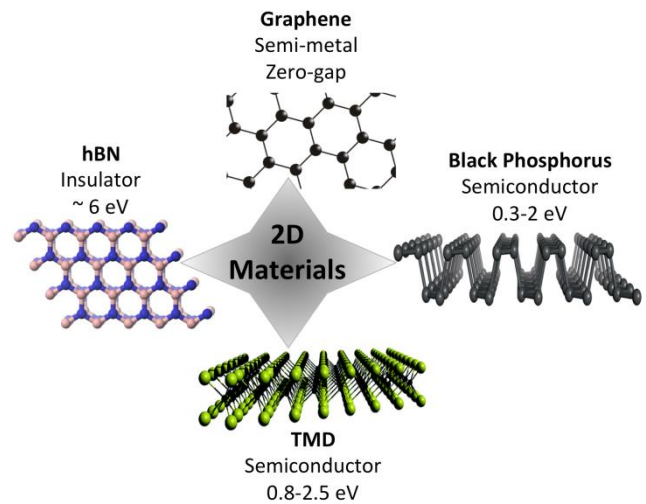

Figure 1 – 2D atomic layered materials offer a variety of band structures towards designing highly functional photon absorption devices. While this emerging material class exhibits some non-classical, more research is needed to fully understand the interplay between transport, light-matter-interaction properties, and mechanical properties such as stress. Abbreviations: see main text.

References
[1] Novoselov, K. S. et al: Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
[2] Mak, K. F. et al: Atomically thin MoS2: A new direct-gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
[3] Tran, V., Soklaski, R., Liang, Y. & Yang, L: Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus. Phys. Rev. B 89, 235319 (2014).
[4] H.S. Lee, S.W. Min, Y.G. Chang, M.K. Park, T. Nam, H. Kim, J.H. Kim, S. Ryu, and S. Im: MoS2 nanosheet phototransistors with thickness-modulated optical energy gap. Nano Lett. 12(7), 3695.
[5] M.Bernardi,M. Palummo, and J.C. Grossman: Extraordinary sunlight absorption and 1 nm-thick

photovoltaics using two-dimensional monolayer materials. Nano Lett. 13(8), 3664 (2013).

[6] Chul-Ho Lee, Gwan-Hyoung Lee, Arend M. van der Zande, Wenchao Chen, Yilei Li, Minyong Han, Xu Cui, Ghidewon Arefe, Colin Nuckolls, Tony F. Heinz, Jing Guo, James Hone & Philip Kim: Atomically thin p–n junctions with van der Waals heterointerfaces. Nature Nanotechnology 9, 676–681 (2014).

[7] Gwan-Hyoung Lee, Young-Jun Yu, Xu Cui, Nicholas Petrone, Chul-Ho Lee, Min Sup Choi, Dae-Yeong Lee, Changgu Lee, Won Jong Yoo, Kenji Watanabe, Takashi Taniguchi, Colin Nuckolls, Philip Kim, and James Hone: Flexible and Transparent MoS2 Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures. ACS Nano 2013 7 (9), 7931-7936.

[8] Sungjin Wi, Hyunsoo Kim, Mikai Chen, Hongsuk Nam, L. Jay Guo, Edgar Meyhofer, and Xiaogan Liang: Enhancement of Photovoltaic Response in Multilayer MoS2 Induced by Plasma Doping. ACS Nano, 2014, 8 (5), pp 5270–5281.

[9] L. Britnell, R.M. Ribeiro, A. Eckmann, R. Jalil, B.D. Belle, A. Mishchenko, Y-J. Kim, R.V. Gorbachev, T. Georgiou, S.V. Morozov, A.N. Grigorenko, A.K. Geim, C. Casiraghi, A.H. Castro Neto, and K.S. Novoselov: Strong light-matter interactions in heterostructures of atomically thin films. Science 340, 1311 (2013).

[10] Mohammad H. Tahersima, Volker J. Sorger: Enhanced Photon Absorption Toward 2-D Material-based Spiral Solar Cell. IOP nanotechnology (accepted 2015)

9. Plasmonics for optical energy conversion

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Status – Plasmonics is the study of plasmons, quasi-particles associated with collective oscillations of electron density in a metal. Plasmon waves can exist and propagate within the bulk or at the surface of a metal, and can be generated by interactions of electromagnetic radiation or an electron beam with the metal. Most of the phenomena associated with waves in general apply to plasmons, perhaps most importantly that of resonance. The energy-momentum dispersion relation for plasmons also differs greatly from that of electromagnetic radiation in vacuum or air, a fact that affords numerous routes to manipulating light-matter interactions. For example, surface-bound plasmons can be localized on size scales far smaller than the wavelength of light in free space, and can propagate (as surface plasmon polaritons, SPP) along channels of comparable small size. In addition, structured media forming metamaterials can be fabricated that incorporate plasmonics to enable new functionalities in nanophotonics and electronics.

Numerous applications have been envisioned and implemented that take advantage of this light confinement and light wave guiding with plasmons. These include molecular and neurosensing, color filtering, nanoscale lithography, lasing, imaging, waveguiding, and the topic of this contribution, energy conversion. The ability to excite plasmons with light means that the energy in light can be transformed and manipulated in tailorable and potentially useful ways [1].

Current and Future Challenges – It can be said that the most significant scientific challenges to increased optical energy conversion efficiency, especially in photovoltaics, are color matching and the "thick-thin" conundrum. The former refers to the spectral nature of sunlight versus the single energy (band gap) nature of semiconductors, and the latter to a thick solar cell being required to maximize optical absorbance while a thin one is advantageous for electron and hole extraction. To date, the series multijunction cell is the only proven solution to the spectral issue [see sections 11,13]. As also described elsewhere in this roadmap, there are several alternative concepts proposed to deal with the problem, from carrier multiplication to hot electron extraction [see sections 5,13] to parallel multijunction (as in a prism) [see sections 11,13] to thermal PV [see sections 15-20]. Likewise for the optical absorber thickness issue, various light-trapping innovations are being conceived and imple-mented to enable high absorption in ultrathin media. These include textured front and/or back electrodes, radial
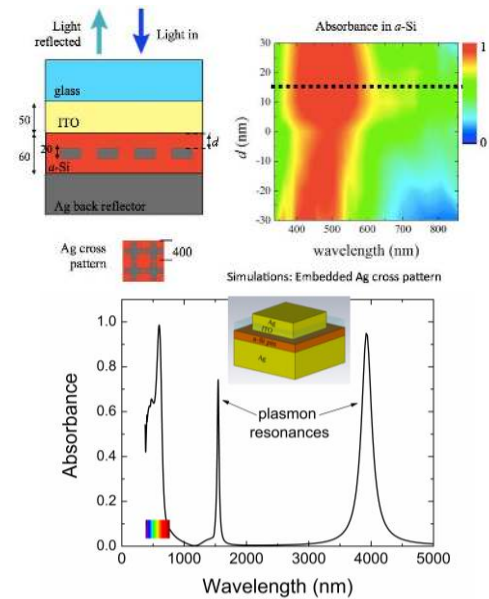

Figure 1 – Examples of plasmonic energy conversion schemes. Top: Plasmonic metal nanopattern embedded in a semiconductor enhances near-field scattering [10]; Bottom: Plasmonic MIM structure where excess energy from hot electrons resonantly couples to IR plasmon modes [9].

junction architectures that strive to decouple the optical and electronic pathlengths by orthogonalizing their respective directions, periodic back reflectors that channel or waveguide light along the plane of a film, thus extending the optical path length, and others. One of the most interesting and perhaps promising new routes to increased light trapping involves plasmonics.

Atwater and Polman [2] gave a thorough review of plasmonics for PV in 2010, discussing how plasmonic metallic nanoparticles/nanostructures could be used to scatter light at oblique angles into a PV absorber, or as nanoantennae to enhance near-field scattering within an absorber, or as waveguides supporting SPP modes at the back reflector, with the evanescent EM wave in the semiconductor at that metal interface enhances carrier generation.

In 2011, a review of plasmonics by Wang, Plummer and Kempa [3] included a chapter which described key plasmonics concepts in solar plasmonics, including Mie resonance, nanotransmission lines, and meta-materials for light trapping, as well as plasmon-induced charge separation for novel class of solar cells.

In 2012, Green and Pillai [4] also briefly summarized the prospects for plasmonics in solar cells, but added to the discussion mentions of possible roles of plasmonic metamaterials and for hot electrons which, in concert, could potentially yield conversion efficiencies well in excess of the Shockley–Queisser limit.

Each of these schemes can be advantageous for reducing the thickness of a PV absorber while maintaining or even increasing optical absorbance. Independently, a great deal of research is underway that uses plasmonics for photocatalytic (water splitting) and photoelectrochemical optical energy conversion. It remains a challenge, however, to successfully implement an energy conversion scheme, aided by device architecture, plasmonic interactions, or a yet-to-be-discovered method, that yields energy conversion greater than that of conventional devices, and of the scale needed to address the global energy challenge.

Advances in Science and Technology to Meet Challenges – A great deal of research is ongoing to improve light collection/trapping in materials, and to use that optical energy for the purpose of energy conversion. An increasing amount of those efforts is devoted to exploiting plasmonics in this realm. Much of the pioneering work of the 19th and early 20th centuries on electromagnetism, from the origins of the diffraction limit, to light scattering in the Mie and Rayleigh regimes, to waveguiding and radio technology, is being revisited on smaller spatial dimensions and optical frequencies in nanostructures, with plasmonic interactions playing a leading role.

Ongoing developments in metamaterials are bringing novel concepts to the field, wherein optical constants (*e.g.* refractive index) are tailorable not only by material composition but by architecture. The combination of plasmonics and metamaterials affords new opportunities for creative nanoscale manipulation of light, and the conversion of electromagnetic energy into usable thermal, electrical or chemical forms.

The various plasmonics concepts can lead to greatly improved photon management materials, including in solar cells, where they address the thick-thin issue. However, the main challenge of solar photovoltaics still remains the color matching problem, *i.e.* the recovery of the energy of hot electrons. This energy is typically lost to heat, due to the rapid times scale of electron-phonon scattering. The expensive multi-junction scheme is the only working scheme today, and aims at eliminating hot electrons altogether by capturing multiple parts of the light spectrum in successively higher band gap semiconductors.

Hot electrons have very short mean-free paths due to phonon emission, of the order of 1 nm. Various schemes have been proposed to recover this hot electron energy. For example, narrow band energy filters at the absorber-electrode contacts were proposed to facilitate the needed isoentropic cooling of the hot electrons, while semiconducting quantum dots were proposed as an active medium of a solar cell to create a phonon bottleneck to slow down phonon emission [5].

In a recent paper [6], a small voltage increase due to the direct recovery of hot electrons was demonstrated in ultrathin amorphous Si photovoltaic junctions, illuminated by laser light at different frequencies in the visible range. Plasmonics could enhance this effect [7, 8].

A specific approach to accomplish this task has been recently proposed [9], based on the fact that electron-*plasmon* scattering can be much faster than electron-*phonon* scattering. Thus, by providing conditions for the former, the hot electron energy could be protected from the latter, and it would remain in the electronic degree of freedom for an extended amount of time. Such hot electron plasmonic protection (HELPP) could be enabled by plasmonic resonators. In one version, these could be embedded directly in a photovoltaic junction [10], as shown in Figure 1 (top). In another, a planar array of plasmonic resonators could be adjacent to a junction, as shown in Figure 1 (bottom). Here, the planar plasmonic resonators also become a part of a metamaterial light trapping structure, which facilitates broadband absorption in the ultrathin absorber. This dual function is evident from the simulated absorption spectrum shown in Figure 1 (bottom), which consists of two sharp plasmonic peaks in the infrared range for the hot electron protection, and a broadband feature in the visible range for light trapping. HELPP effectively increases the lifetime of hot electrons, and thus increases the probability of their arrival at the collector in the "hot" state. Successfully implemented, this scheme would lead to increased open circuit voltage with no loss of current.

Concluding Remarks – While most proposed plasmonic energy conversion concepts focus on light trapping, leading to a significant improvement in *e.g.* solar performance, the main challenge is to solve the color matching problem: recovery of the energy of hot electrons usually lost to heat. Novel plasmonic concepts, such as the HELPP mechanism, offer possible solutions.

References
[1] Boriskina, S.V., Ghasemi, H. and Chen, G., Plasmonic materials for energy: From physics to applications, Mat. Today 6, 375-386 (2013).
[2] Atwater, H.A. and Polman A., Plasmonics for improved photovoltaic devices, Nat. Mater. 9, 205–213 (2010).
[3] Wang, Y., Plummer, E.W. and Kempa K., Foundations of plasmonics, Adv. Phys. 60, 799-898 (2011).
[4] Green, M.A. and Pillai, S., Harnessing plasmonics for solar cells, Nat. Photonics, 6, 130–132 (2012).
[5] Ross, R.T. and Nozik, A.J., Efficiency of hot-carrier solar energy converters, J. Appl. Phys. 53, 3813-

3818 (1982); Nozik, A.J., Quantum dot solar cells, Physica E 14, 115-120 (2002).

[6] Kempa, K., et al., Hot electron effect in nanoscopically thin photovoltaic junctions, Appl. Phys. Lett. 95, 233121 (2009).

[7] Brongersma, M.L., Halas, N.J. and Nordlander, P., Plasmon-induced hot carrier science and technology, Nat. Nanotechnol. 10, 25–34 (2015).

[8] Clavero, C., Plasmon-induced hot-electron generation at nanoparticle/metaloxide interfaces for photovoltaic and photocatalytic devices, Nat. Photonics 8, 95–103 (2014).

[9] Kempa, K., Plasmonic protection of the hot-electron energy," Phys. Stat. Sol. RRL 7, 465–468 (2013); Kong, J. et al., Toward a hot electron plasmonic solar cell, Opt. Expr. (2015, accepted)

[10] Ye, F., Burns M.J., and Naughton, M.J., Embedded metal nanopatterns as a general scheme for enhanced broadband light absorption, Phys. Stat. Sol. (A) 212, 561-565 (2015); Embedded metal nanopatterns for near-field scattering-enhanced optical absorption, ibid 209, 1829-1834 (2012).

10. Light rectification using an optical antenna and a tunneling diode – Mario Dagenais

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Status – The integration of an optical antenna with a tunneling diode with proper impedance matching leads to what is now called a rectenna [1]. This device allows the capture of an optical signal falling on an optical antenna and the efficient rectification of this signal by the tunneling diode. The demodulator of choice for the rectenna is the metal-insulator-metal (MIM) tunnel diode [2]. Schottky diodes are also a candidate for the rectifier but they typically operate at lower frequencies than MIM diodes. The response time of the rectenna consists of several contributions: 1) the collective response of the conduction electron that establish the AC bias, which extend to frequencies well beyond the UV, 2) the tunneling time for electrons to cross the gap region before field reversal, and 3) the electrodynamical (parasitic) response of the junction to the changing field, in particular, the RC response time.

The antenna is modeled as a voltage source V_A in series with a resistance R_A and the MIM diode is modeled as a resistor R_D in parallel with a capacitor C_D. Efficient transfer of power from the antenna to the load R_D requires matching R_A with R_D and keeping the time constant $\tau = (R_A \parallel R_D) C_D$ much below the time period of the source V_A [3]. For a parallel plate capacitor, the time constant $\tau = R_D C_D$ is independent of the diode area and is determined by the composition of the MIM diode. Assuming a breakdown current density of 10^7 A/cm^2 at 0.1 V and a dielectric constant $\varepsilon = 1$ at a thickness of 10 nm, a time constant $\tau = 10^{-15}$s is extracted, which is too large for coupling at visible wavelength. It is then concluded that a planar MIM diode, represented by a parallel plate capacitor, would operate well in the infrared, say up to 30 THz, but would not operate in the visible. The extension of the planar MIM diode to the visible is a challenge. By contrast, point-contact devices (i.e. whisker diodes) have demonstrated frequency response up to frequencies in the green part of the visible spectrum but they are very irreproducible and hard to use. The asymmetrical, non-planar geometry of the whisker, together with the flat anode, are essential requirements for increasing the cut-off frequency of the diode. The present challenges include realizing these structures in a reproducible and stable way, using well-established nano-fabrication techniques, and scaling up these structures to large arrays.

Current and Future Challenges – It was recently demonstrated that the response time for a point contact with a spherical tip is proportional to $A^{-1/4}$, where A is the area of the junction [4]. This implies that it is
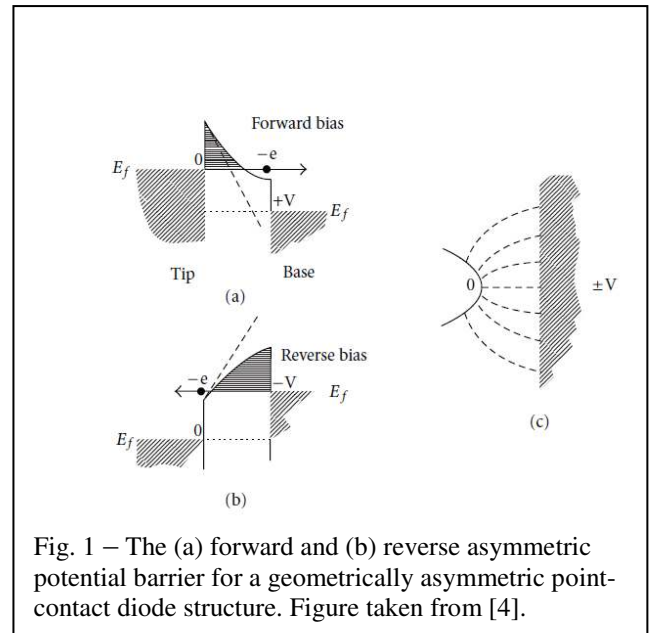

Fig. 1 – The (a) forward and (b) reverse asymmetric potential barrier for a geometrically asymmetric point-contact diode structure. Figure taken from [4].

possible to decouple resistance and capacitance and appreciably improve the response time of the diode, possibly to the visible frequencies of the solar spectrum. Rectification requires an imbalance between the forward and reverse currents circulating during the positive and negative cycles of the AC potential at the junction. An electrical asymmetry in the I-V characteristics can be obtained using various approaches including material asymmetry, thermal asymmetry, and geometric asymmetry. By applying a bias, efficient rectification can be realized for detector applications. However, for energy harvesting applications, it is necessary to operate the diode at zero external bias. The geometric asymmetry diode (see Fig. 1) was demonstrated in [6] and it allowed energy harvesting at zero external bias. A sharply pointed planar triangular tip emitter incident on the boundary of a square receiver provides electric field asymmetry (see Fig. 2) [2]. When the square is biased positively, the electric field line density incident on the triangular tip is enhanced by the lightning rod effect. The inverse tunneling current is much reduced because of the lower electric field at the surface of the flat electrode. Four parameters are typically used to characterize the rectification efficiency. They are: 1) the differential junction resistance $R = dV_{DC}/dI_{DC}$, 2) the nonlinearity $I'' = d^2I_{DC}/dV^2_{DC}$, 3) the sensitivity or responsivity

$$S = \frac{1}{2} \frac{d^2 I_{DC}/dV^2_{DC}}{dI_{DC}/dV_{DC}},$$ and 4) the quantum efficiency

$$\eta_q = \frac{\hbar\omega}{e} S.$$ The equations for R and S are altered in a quantum description of the photon assisted tunneling. This is required when the incident optical photon energy on the antenna corresponds to $V_{nonlinear}$ of order

100 meV, typical of low-barrier metal/insulator/metal diodes, and is typical of metal-insulator-metal barrier height. In this quantum description, the classical values of resistance and the responsivity decreases as the photon energy increases [7]. The maximum achievable conversion efficiency (ratio of output dc power to the input ac power) for monochromatic illumination is 100%. For broadband illumination, the diode operating voltage plays the role that bandgap plays in conventional solar cells and efficiencies approaching the Shockley-Queisser limit are expected [8]. Furthermore, because sunlight is spatially coherent only over a limited area, concentration of the incident light is limited [see section 12]. A coherence of 90% for a broadband solar spectrum is reachable only for a circle of radius 19 μm [9].
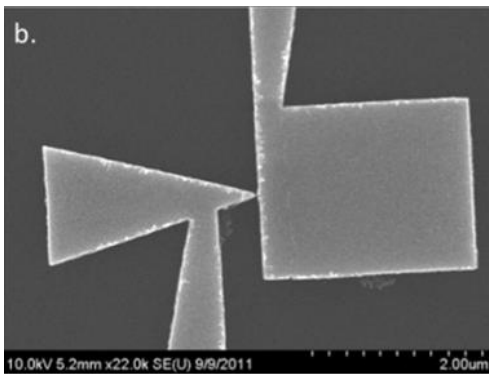

Fig. 2 – SEM micrograph of Ni/NiO$_x$/Ni geometrically asymmetric tunneling diode/nanoantenna

Advances in Science and Technology to Meet Challenges – The power conversion efficiency in a rectenna depends on 1) the efficiency of the coupling of incident radiation to the antenna, which depends on the antenna radiation pattern as well as its bandwidth and the coherence of the light, 2) the efficiency with which the collected energy propagates to the junction and is governed by resistive losses at high frequencies in the antenna, 3) the coupling efficiency between the antenna and the diode, which depends on impedance matching, and 4) the efficiency of rectifying the power received in the diode, which is related to the diode responsivity. It is also important to consider the use of noble metals and plasmonic resonances on the field enhancement and rectification properties on a tunneling junction [see section 9]. Recent results demonstrate the importance of the plasmon frequency on both the material and the geometry of the tip which could be used to control the frequency at which the junction is most efficient for the rectification of optical signals [4]. At optical frequencies, the classical skin depth in metals is of order 30 nm and optical losses can be very large. Characterization of nanojunctions as a function of wavelength, polarization, materials, is required for optimizing the rectenna. The difficulty of producing arrays of nanometer gap junctions over areas of order cm^2 has to be studied. By using constructive interference, it is possible to coherently combine the electric fields from the different antennas of an array. This would allow the control of the antenna array far field. This needs to be studied in more details. Tips of radius of a few nm's have to be produced in order to get very high frequency response. Ultimately, the junctions will be limited by dielectric breakdown. More research needs to focus on this issue.

Concluding Remarks – Rectennas have the potential of converting solar energy to electrical power all the way from the infrared to the visible using arrays of potentially low cost devices with conversion efficiencies similar to photovoltaic devices. As discussed, geometrically asymmetric diodes can rectify radiation all the way to the visible and therefore appears most promising. Rectennas can also be used for beaming monochromatic infrared and visible power with detection efficiencies approaching 100%. Another potential application of this technology is for waste heat harvesting in the IR if the coherence area of the infrared radiation is appropriately selected. Rectennas can use nanoimprints and roll-to-roll technologies for reducing the manufacturing cost. So far, low efficiency rectennas (of order 1%) have been demonstrated in the IR. Much work obviously remains to be done to demonstrate the full potential of this technology.

References
[1] G. Moddel and S. Grover, Editors, "Rectenna Solar Cells", (Springer, New York, 2013), pp. 398.
[2] F. Yesilkoy, S. Potbhare, N. Kratzmeier, A. Akturk, N. Goldsman, M. Peckerar, and M. Dagenais," A mid-IR antenna integrated with a geometrically asymmetrical metal-insulator-metal rectifying diode", in Rectenna Solar Cells, edited by G. Moddell and S. Grover, (Springer, New York, 2013), pp. 163-188.
[3] S. Grover and G. Moddel, "Applicability of metal/insulator/metal (MIM) diodes to solar rectennas", IEEE J. Photovoltaics, 1, 78 (2011).
[4] N.M. Miskovsky, P.H. Cutler, A. Mayer, B.L. Weiss, B. Willis, T.E. Sullivan, and P.B. Lerner, "Nanoscale devices for rectification of high frequency radiation from the infrared through the visible: a new approach", J. Nanotechnology, 2012, 19 pages, doi: 10.1155/2012/512379.
[5] H.Q. Nguyen, P.H. Cutler, T.E. Feuchtwang, Z.-H. Huang, Y. Kuk, P.J. Silverman, A.A. Lucas, and T.E. Sullivan, "Mechanisms of current rectification in an STM tunnel junction and the measurement of an operational tunneling time", IEEE Trans. Electron Devices, 36, 2671 (1989).
[6] M. Dagenais, K. Choi, F. Yesilkoy, A.N. Chryssis, M. C. Peckerar, "Solar spectrum rectification using

nano-antennas and tunneling diodes", Proc. SPIE, vol. 7605, article #76050E, (2010).

[7] S. Grover, S. Joshi, and G. Moddel, "Quantum theory of operation for rectenna solar cells", J. Phys. D: Appl. Phys. 46, 136106 (2013).

[8] S. Joshi and G. Moddel, "Efficiency limits of rectenna solar cells: theory of broadband photon-assisted tunneling", App. Phys. Lett. 102, 083901 (2013).

[9] H. Mashaal and J. M. Gordon, "Fundamental bounds for antenna harvesting of sunlight", Opt. Lett. 36, pp. 900-902, (2011).

11. Full solar spectrum conversion via multi-junction architectures and optical concentration

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Status – Significant advances have been made in research to improve the performance of single-junction photovoltaic devices. Currently, the best silicon and GaAs devices have achieved efficiencies of 25.6% and 28.8%, respectively [1] [see sections 2,4]. The realization of significant further enhancements in the efficiencies of photovoltaic energy conversion, however, resorts to multi-junction (MJ) architectures using semiconductor materials with subcell bandgaps tuned to target different portions of the solar spectrum, in order to minimize carrier thermalization losses and increase spectrum coverage to exceed the Shockley-Queisser limit [2]. In theory, a MJ cell can achieve an efficiency as high as 86.8% with an infinite number of junctions [3] (a value lower than the Landsberg limit [4] due to entropy losses in light absorption), and a number of different cell designs have been intensively explored by the photovoltaic research community as means through which such forms of performance enhancement can be realized. These include most notably devices that embed the semiconductor elements in the form of multi-junction solar cell stacks [5], and to a lesser degree optical approaches involving various forms of spectrum splitting [6] [see also section 13]. In the first design, the subcells are either epitaxially or mechanically stacked together in the order of decreasing bandgaps to divide the incident sunlight using the absorption of the subcells [see also section 3]. In the second approach, separate optics (e.g. prisms, holograms, and dielectric band-pass filters) are used to split the solar spectrum and direct different portions to the relevant subcell. It has been persuasively argued that both designs would benefit from high geometric concentration of the solar irradiance as one means to both offset the high materials costs encumbered by the III-V semiconductor device elements and to enhance the system power-conversion efficiency. To date, cell stacking designs have achieved the highest benchmark performances in solar energy conversion, with world-record efficiencies of MJ cells reaching 46.0% with a 4-junction design (InGap/GaAs//GaInAsP/GaInAs) under 508 suns [1]. Exemplary recent progress includes a report from our group of 43.9% efficient quadruple junction, four terminal microscale solar cells that were fabricated by mechanical stacking of a top 3-J device onto a bottom Ge cell via transfer-printing-based assembly [7].

Current and future challenges – For epitaxially-grown MJ devices, the difficulty of sustaining lattice matching through multiple layers of growth limits the materials selections that are available for use in each subcell and thus directly restricts achievable limits for device performance. Mechanically-stacked devices, on the other hand, can be fabricated via high temperature wafer bonding [8] to circumvent this issue, but still carries a requirement for current matching at the electrically-conducting interfaces, which is difficult to realize as the number of subcells increase to sub-divide the solar spectrum. Alternatively, insulating adhesives can be used between mechanically stacked subcells to enable multi-terminal connections and in this way avoid the need for current matching. These interfaces need to be carefully designed to minimize reflection losses, as well as manage heat flow and thermal-mechanical stresses at high optical concentration [7]. Additional electro-optical challenges exist for the material used in each subcell. For example, a top wide-bandgap subcell (i.e. E_g > 1.4 ev) generally cannot be intrinsically doped to a sufficiently high level (>10^{19} cm^{-3}) to enable efficient carrier collection under high-irradiance concentration; it requires incorporation of highly doped, low bandgap materials that either degrade its optical transparency for low energy photons or complicated back contact grid configurations [5].

It has been noted that the limitations associated with stacked MJ devices can be tackled in principle by employing external optical components to split and distribute the solar radiation to an array of spatially separated subcells [9]. By decoupling material compatibility from bandgap optimization, this approach also enables MJ designs with larger numbers of subcells and, thus, higher theoretical efficiencies. As the cell fabrication steps are reduced to providing a set of single-junction devices, simplified process flows for the semiconductor components are possible [see sections 2,7]. The common proposed optical designs include holographic gratings and wavelength selective mirrors (e.g. multilayer dielectric Bragg stacks). Their practical use, however, is hindered by the formidable requirements for high-optical quality as well as the complexity of the optical designs needed to achieve competitive system-level efficiencies.

The high cost of III-V materials, especially in MJ cell contexts, likely necessitates a high optical-concentration design to achieve commercial viability [see section 12]. Optical losses figure importantly in all forms of concentrator PV designs. Stacked cells, for example, are subject to significant Fresnel losses (e.g. 12% of incident photons are lost to reflection before reaching the solar cells for a system with three glass/air interfaces) that limit their optical (and thus

power conversion) efficiencies. Broadband anti-reflection (AR) coatings would afford an ideal solution, but materials that can span the refractive index range needed to mitigate these effects have yet to be developed. The use of common light trapping designs on the PV cells also become more complex, as they can scatter light and otherwise limit the broad-spectrum performance of high-concentration optics [see section 3]. Geometric solar concentrators (GSC) also require solar tracking, and even more significantly do not utilize diffuse light—a significant component of the solar spectrum. (The diffuse component is 15% in AM1.5G illumination; most locations in the United States having 24% to 50% diffuse sunlight [10].)

Advances in science and technology to meet challenges – *(1) Light management within and between subcells.* It has been shown in single junction devices, that high external radiation efficiencies (ERE) and enhanced photon recycling are crucial for high PV performance (as demonstrated by the world record GaAs device, where the radiatively emitted photons are reflected by a metal back surface rather than absorbed by the substrate) [11, 12] [see section 4]. Likewise, MJ devices with intermediate reflectors that enhance ERE and photon recycling would improve the V_{oc} for each subcell (Figure 1), although these reflectors also need to transmit subbandgap photons for the next cell. Different designs have been examined theoretically that provide such effects, such as stacks spaced by an airgap coupled with AR coatings as the intermediate reflector in-between subcells [13]. The elements of this design have been demonstrated experimentally using microscale solar cells stacked onto pre-patterned airgap spacers using a soft-transfer-printing technique [14]. The opportunities for progress have also been demonstrated theoretically in the design of a high performance spectrum-splitting PV system that uses polyhedral specular reflectors coupled to spatially separated devices to enhance both photon recycling within a subcell and radiative coupling between them [15].
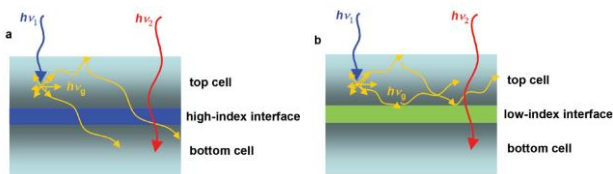
Figure 1 − Illustrations demonstrating photon dynamics in a MJ device (reproduced from ref [13]). (a) No photon recycling: the radiative emission from the top cell is coupled to the bottom cell. (b) With photon recycling: using a low index interface as an intermediate reflector, the ERE and V_{oc} of the top cell are enhanced.

(2) Improving the optical efficiencies of GSC. There exist numerous opportunities to improve the performance of concentrator PV systems. Providing
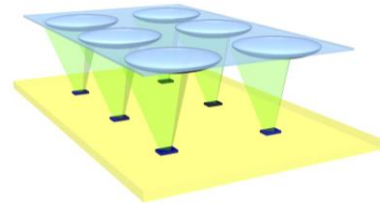
Figure 2 − Schematic design of a hybrid concentration system with an embedded microscale solar cell module, both the device and the luminescent waveguide can be configured as a multi-junction architecture for full spectrum conversion.

improved broadband antireflection coatings (e.g. porous films with subwavelength features to avoid scattering) forms one obvious direction in research to reduce the Fresnel losses associated with concentrating optics. The development of strategies that would allow the utilization of diffuse light within a concentrator PV design is also of significant interest. We might envision, for example, the coupling of a GSC with a luminescent solar concentrator (LSC), wherein diffuse radiation striking the backplane can be absorbed by the luminophore and down-converted into total internal reflection modes that are directed to the embedded photovoltaic device elements. A possible geometry for such a system suggested by elements of our past work is one embedding arrays of microscale solar cells directly in the LSC waveguide (Figure 2), such that, in addition to diffuse light conversion, the direct illumination from the sun can be concentrated at the top surface of the devices using a GSC with a higher concentration ratio and optical efficiency [16, 17]. We have shown that quantum dot luminophores (QD) [see also sections 5,6] are particularly advantageous for use in such microcell LSC arrays as compared to traditional organic dyes, as they have high quantum yields, large (and tunable) Stokes shifts for reduced reabsorption losses, and better long-term photo-stability. Their narrow emission peak also facilitates photonic designs to better trap/ manage the luminescent photons to improve optical efficiency [17]. It is also of particular interest to note that high optical efficiency LSCs may engender specific capabilities for high performance CPV designs that would be transformational, specifically to obviate the need for solar tracking as well as the intriguing possibility that they might enable new approaches to spectrum splitting using discrete subcell arrays that can achieve efficiencies approaching those associated with monolithic MJ cell stacks.

Concluding remarks − Multi-junction architectures are required to achieve full spectrum conversion and surpass the Shockley-Queisser limit. Concentration is advantageous in a MJ system in both improving their efficiency and cost. This perspective outlines new materials, optical integration strategies, and approaches to spectrum splitting that beget new opportunities

through which the grand challenge of full-spectrum conversion might be realized.

References

[1] M. A. Green, K. Emery, Y. Hishikawa *et al.*, "Solar cell efficiency tables (Version 45)," Progress in Photovoltaics: Research and Applications, 23(1), 1-9 (2015).

[2] W. Shockley, and H. J. Queisser, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells," Journal of Applied Physics, 32(3), 510-519 (1961).

[3] A. D. Vos, "Detailed balance limit of the efficiency of tandem solar cells," J. Phys. D: Appl. Phys., 13, 839 (1980).

[4] P. T. Landsberg, and G. Tonge, "Thermodynamic energy conversion efficiencies," Journal of Applied Physics, 51(7), R1-R20 (1980).

[5] H. Cotal, C. Fetzer, J. Boisvert *et al.*, "III-V multijunction solar cells for concentrating photovoltaics," Energy & Environmental Science, 2(2), 174-192 (2009).

[6] A. G. Imenes, and D. R. Mills, "Spectral beam splitting technology for increased conversion efficiency in solar concentrating systems: a review," Solar Energy Materials and Solar Cells, 84(1–4), 19-69 (2004).

[7] X. Sheng, C. A. Bower, S. Bonafede *et al.*, "Printing-based assembly of quadruple-junction four-terminal microscale solar cells and their use in high-efficiency modules," Nat Mater, 13(6), 593-598 (2014).

[8] K. Derendorf, S. Essig, E. Oliva *et al.*, "Fabrication of GaInP/GaAs//Si Solar Cells by Surface Activated Direct Wafer Bonding," Photovoltaics, IEEE Journal of, 3(4), 1423-1428 (2013).

[9] A. Polman, and H. A. Atwater, "Photonic design principles for ultrahigh-efficiency photovoltaics," Nat Mater, 11(3), 174-177 (2012).

[10] W. Marion, and S. Wilcox, [Solar radiation data manual for flat-plate and concentrating collectors] National Renewable Energy Laboratory, (1994).

[11] O. D. Miller, E. Yablonovitch, and S. R. Kurtz, "Strong Internal and External Luminescence as Solar Cells Approach the Shockley-Queisser Limit," Photovoltaics, IEEE Journal of, 2(3), 303-311 (2012).

[12] E. D. Kosten, B. M. Kayes, and H. A. Atwater, "Experimental demonstration of enhanced photon recycling in angle-restricted GaAs solar cells," Energy & Environmental Science, 7(6), 1907-1912 (2014).

[13] V. Ganapati, H. Chi-Sing, and E. Yablonovitch, "Air Gaps as Intermediate Selective Reflectors to Reach Theoretical Efficiency Limits of Multibandgap Solar Cells," Photovoltaics, IEEE Journal of, 5(1), 410-417 (2015).

[14] X. Sheng, M. H. Yun, C. Zhang *et al.*, "Device Architectures for Enhanced Photon Recycling in Thin-Film Multijunction Solar Cells," Advanced Energy Materials, 5(1), 1400919 (2015).

[15] C. N. Eisler, Z. e. R. Abrams, M. T. Sheldon *et al.*, "Multijunction solar cell efficiencies: effect of spectral window, optical environment and radiative coupling," Energy & Environmental Science, 7(11), 3600-3605 (2014).

[16] J. Yoon, L. Li, A. V. Semichaevsky *et al.*, "Flexible concentrator photovoltaics based on microscale silicon solar cells embedded in luminescent waveguides," Nat Commun, 2, 343 (2011).

[17] N. D. Bronstein, L. Li, L. Xu *et al.*, "Luminescent Solar Concentration with Semiconductor Nanorods and Transfer-Printed Micro-Silicon Solar Cells," ACS Nano, 8(1), 44-53 (2013).

12. Advanced solar concentrators – Jeffrey M Gordon,
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Status – Concentrating sunlight has fascinated people since time immemorial [1]. Heat production and electricity generation comprise the main current applications (unorthodox uses include nanomaterial synthesis [2] and medical surgery [3]). Generally, solar concentration is motivated by cost and efficiency. Cost because expensive receivers are largely replaced by inexpensive optics. Solar *thermal* efficiency benefits from markedly reducing heat-loss area. Photovoltaic conversion efficiency can increase linearly with Log(concentration) at low series resistance [see also section 11].

"Advanced" refers to concentrators that approach the thermodynamic limit for the relation between flux concentration C and acceptance half-angle θ_a, *at high collection efficiency*: $C \sin^{d-1}(\theta_a) \leq n^{d-1} \sin^{d-1}(\theta_e)$, where n is the refractive index in the concentrator (air, but occasionally a transparent dielectric for photovoltaics), θ_e is the maximum half-angle irradiating the absorber, and d is the dimensionality [4-6]. Minimally, θ_a is the convolution of the sun's angular radius (0.27°) with manufacturing, installation and tracking imperfections. Maximally (for static low-concentration collectors), θ_a is the angular range from which beam radiation is collected over the day. The familiar solutions of spherical-cap or Fresnel lenses, and parabolic or Fresnel mirrors, that have dominated solar technologies to date fall far short of the thermodynamic limit [4-6].

Advanced concentrators range from static 2D systems ($\theta_a \approx 25\text{-}90°$), to single-axis tracking line-focus systems ($C \approx 5\text{-}100$), and dual-axis tracking point-focus systems ($C \approx 100\text{-}100,000$). Nonimaging optics uniquely provides static designs that approach the thermodynamic limit [4-6]. Some enjoyed commercial realization (Fig. 1a). The higher concentration domain is still dominated by parabolic and Fresnel mirrors, and Fresnel lenses, although a variety of advanced nonimaging second-stage concentrators have been developed [4-6]. The Simultaneous Multiple Surface (SMS) method [4,5] was the first to spawn advanced concentrators that were both ultra-compact and could accommodate a sizable gap between the absorber and the optic. The nonimaging strategy maps incident extreme rays to the extremes of the absorber [4,5].

Advanced aplanatic concentrators [7] opened new vistas, recently adopted for photovoltaics (Fig. 1b). The *imaging* aplanatic strategy (viable for $\theta_a \leq \sim 2°$) completely eliminates spherical aberration and coma [7], while admitting ultra-compact, pragmatic optics.
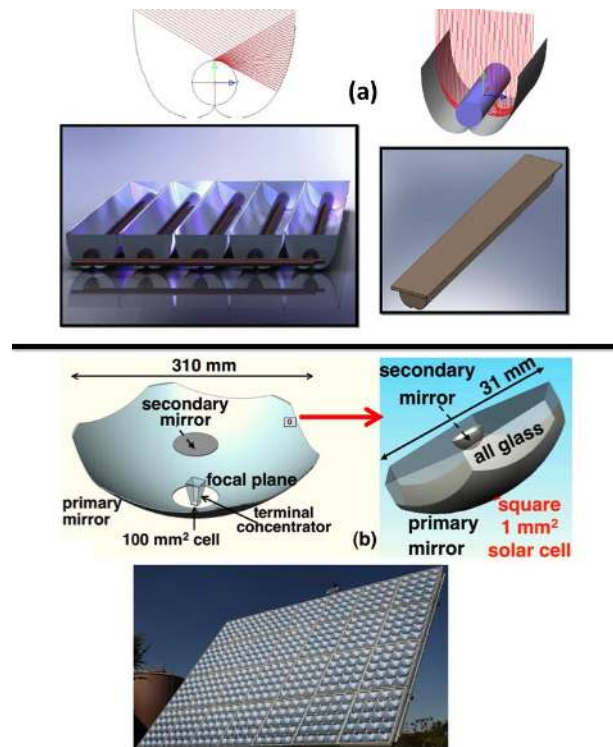

Figure 1 – (a) Sample advanced *static* nonimaging concentrator with an evacuated tubular absorber, for steam production. (b) Two generations of advanced aplanatic concentrator for photovoltaics, first air-filled for 1 cm² cells, then transitioning to glass-filled for 1 mm² cells, plus a photo of an installed 15 kW$_{peak}$ array comprising the former.

Current and Future Challenges – For photovoltaics, current challenges subsume (a) ultra-miniaturization that enhances the feasibility of SMS and aplanatic concentrators (especially dielectric-filled units), and (b) spectrum-splitters that take better advantage of the spectral conversion of separate solar cells. Another tack is quasi-stationary high-concentration optics that would markedly simplify and downsize solar trackers via the use of either: (1) light guides (which have remained at the developmental level due, in part, to substantial optical losses), and (2) *spherical* gradient-index (GRIN) lenses (Fig. 2a), which await accurate high-volume fabrication methods. A recent GRIN advance demonstrated lens refractive index profiles for off-the-shelf solar-transparent materials, with efficient performance that approaches the thermodynamic limit [8]. The prior conventional wisdom had been that only the refractive index profiles of eponymous Luneburg lenses (with refractive indices, for solar frequencies, for which no materials have yet been identified) could achieve the objectives [8].

Another tantalizing new direction is solar aperture rectifying antennas (rectennas), predicated on exploiting the partial spatial coherence of sunlight with micro-concentrators, nano-antennae and ultra-fast rectifiers (AC to DC conversion) [see section 10] [9]. The topic of light rectification is elaborated in Section 08b of this article. Solar aperture rectennas have been shown to possess fundamental limits (for conversion

efficiency) that exceed those of solar thermal and concentrating photovoltaics, but require micro-concentrators within the spatial coherence area of solar beam radiation, to wit, radii of the order of tens of microns [9] (Fig. 2b), such that C is of the order of 10^3. Because phase-conserving optics are needed, devices should approach perfect imaging and hence the thermodynamic limit (Fig. 2c).

Advances in Science and Technology to Meet Challenges – The technological advances needed to address these challenges fall mainly into two categories: micro-fabrication and materials. For the latest miniaturized concentrator solar cells with linear dimensions of ~0.5 mm, all-dielectric optics that are unfeasible for conventional cells with linear dimensions of the order of a cm (simply due to the mass per aperture area) present promising alternatives. This will require integrated production methods (micro-modularity) with solar cells, micro-optics, wiring, bypass diodes and heat sinks comprising a single manufactured unit. Accurate micro-optical fabrication both for lenses and highly reflective specular mirrors will be essential. This also necessitates the precise and reproducible fabrication of sheets comprising thousands of photovoltaic mini-concentrators per m^2 of collection area.

For solar rectennas, this will correspond to the order of a billion aperture rectennas per m^2 of collection area. These units will require the development of efficient *broadband* nanoantennas and broadband ultrafast rectifiers (a bandwidth of the order of 10^6 GHz).

Although viable spherical GRIN lenses have been produced by the trillions for millions of years (chiefly fish eyes), the development of accurate, robust and affordable fabrication procedures has proven elusive, albeit with recent encouraging progress [10]. The newly discovered GRIN solutions for available materials can also be tailored to fabrication constraints such as an extensive constant-index core and constant-index shell regions [8]. Lens diameters will vary from the order of cm (for concentrator photovoltaics) to tens of microns for solar aperture rectennas.

Finally, specifically for the *optical* aspects of solar thermal power conversion, the challenge shifts to the development of superior (and robust) selective coatings (i.e., high solar and low infrared emissivity) at progressively higher temperatures that give rise to higher turbine efficiencies [see sections 15,17]. This relates both to line-focus (evacuated) receivers in quest of efficient operation above ~700 K, as well as to point-focus (non-evacuated) receivers aiming to operate at temperatures exceeding 1000 K.

Concluding Remarks – Achieving ultra-efficient solar conversion could basically be solved if *efficient and*

feasible methods could be found to convert broadband solar to narrowband radiation, which could then be exploited by a plethora of radiation converters (including those from physical optics such as diffractive and holographic elements, rectifying antennas, etc., that are insufficiently efficient due to the narrow spectrum they can accommodate). Proposals of photovoltaic up conversion and down conversion notwithstanding [see sections 13-18], current proposals are far below the required performance. Hence, in the foreseeable future, the focus will likely be on the types of nonimaging and aplanatic optics, gradient-index optics, and micro-modularity (permitting optics precluded by common large-absorber collectors) that not only can raise solar conversion efficiency, but can render them more practical and amenable to large-volume production.
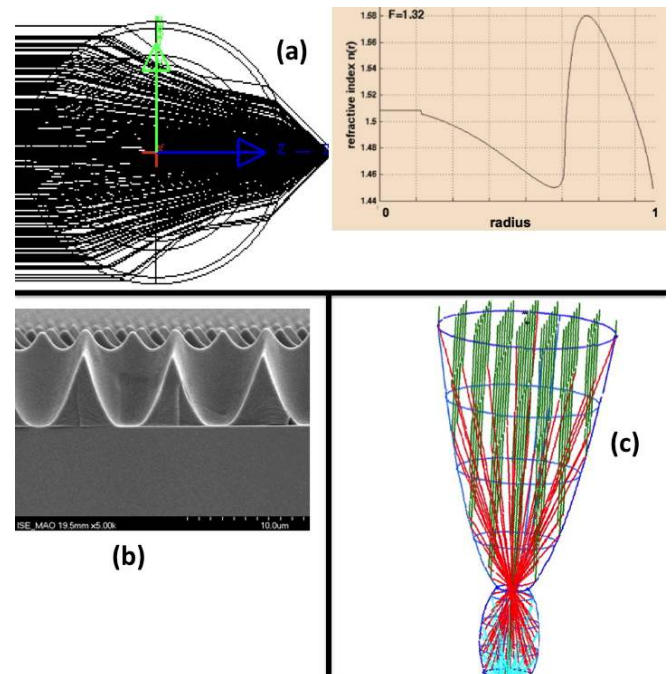

Figure 2 – (a) Illustration of new solutions (for refractive index as a function of radius) for spherical GRIN lenses accommodating refractive indices available for off-the-shelf materials that are transparent in the solar spectrum. The substantial constant-index core region facilitates lens fabrication [8]. This unit-radius ultra-high-concentration f/0.66 lens was raytraced for the full solar spectrum and the extended solar disk. (b) Electron micrograph showing current state-of-the-art fabrication for micro-concentrators. (c) A candidate high-concentration aplanat [7] that could be used in solar aperture rectennas [9]. The aplanat can be dielectric-filled, and satisfies total internal reflection.

References
[1] J. Perlin, *Let It Shine: The 6,000-Year Story of Solar Energy*, New World Library: Novato, CA (2013).
[2] H. Lu, B.C.Y. Chan, X. Wang, H.T. Chua, C.L. Raston, A. Albu-Yaron, M. Levy, R. Popovitz-Biro, R. Tenne, D. Feuermann, J.M. Gordon, "High-yield synthesis of silicon carbide nanowires by solar and lamp ablation", *Nanotechnology* **24**, 335603 (2013).

[3] J.M. Gordon, D. Feuermann, M. Huleihil, S. Mizrahi, R. Shaco-Levy, "Surgery by sunlight on live animals", *Nature* **424**, 510 (2003).

[4] A. Rabl, *Active Solar Collectors And Their Applications*, Oxford U. Press: New York (1985).

[5] R. Winston, J.C. Miñano, P. Benítez, *Nonimaging* Optics, Elsevier: Oxford (2005).

[6] J. Chaves, *Introduction To Nonimaging Optics*, CRC Press: Boca Raton, FL (2008).

[7] J.M. Gordon, "Aplanatic optics for solar concentration", *Opt. Express* **18**, A41-A52 (2010).

[8] P. Kotsidas, V. Modi, J.M. Gordon, "Gradient-index lenses for near-ideal imaging and concentration with realistic materials", *Opt. Express* **19**, 15584-15595 (2011).

[9] H. Mashaal, J.M. Gordon, Basic limit for the efficiency of coherence-limited solar power conversion", *Opt. Lett.* **39**, 5130-5133 (2014).

[10] S. Ji, K. Yin, M. Mackey, A. Brister, M. Ponting, E. Baer, "Polymeric nanolayered gradient refractive index lenses: technology review and introduction of spherical gradient refractive index ball lenses", *Opt. Eng.* **52**, 112105 (2013).

13. Spectral splitting and non-isothermal solar energy conversion – Svetlana V Boriskina
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Status – The broadband nature of thermal radiation – including sunlight and that of terrestrial thermal sources – imposes limitations on the light-to-work efficiency of the whole-spectrum energy converters[1]. Quantum conversion platforms such as photovoltaic (PV) cells are unable to harvest the low-energy photons and convert the high-energy ones very inefficiently [see sections 2,3]. In turn, thermal energy converters with blackbody receivers suffer from re-emission losses at high temperatures and require high level of solar concentration to overcome such losses [see section 12]. Achieving high optical concentration (e.g. by using a large heliostat field) may not only be costly, but also introduces additional loss mechanisms, which negatively impact overall system efficiency.

Sorting photons by their energies and processing them separately helps to increase the light-to-work conversion efficiency. The most explored approach to spectral splitting is based on using multi-junction PV cell stacks (Figs. 1a), where the wide-bandgap top cells absorb high-energy photons, while the lower-energy ones are transmitted through to the narrow-bandgap cells at the bottom of the stack [see section 11]. The stacked spectral splitters/converters can also incorporate catalytic platforms to harvest to UV light and thermal receivers to absorb low-energy IR photons. Yet, efficient stacking and electrical wiring of several converters is challenging, especially in hybrid configurations that include converters with different operating temperatures, which might require thermal insulation between the PV and thermal receivers.

To address these issues, cascade reflection and external spectrum splitting schemes are being actively explored, which make use of perfect and dichroic mirrors, holograms, dielectric prisms, polychromats, etc[2,3]. (Fig. 1b,c). This shifts the R&D focus from the PV material design and fabrication issues to the development of efficient optical elements. Even traditional stacked PV configurations can benefit from adding photon-management elements such as embedded wavelength-selective filters for photon trapping and recycling[4].

Current and Future Challenges – The solar radiation is dilute and is even further diluted by spectral splitting, which in turn reduces the energy conversion efficiency, especially for the solar-thermal converters. Although spectral splitters can be combined with external solar concentrators, fully integrated platforms may help to reduce optical losses and provide cheaper and more compact technological solutions. Spectral-splitting holograms can simultaneously provide some optical concentration. Higher concentration can be
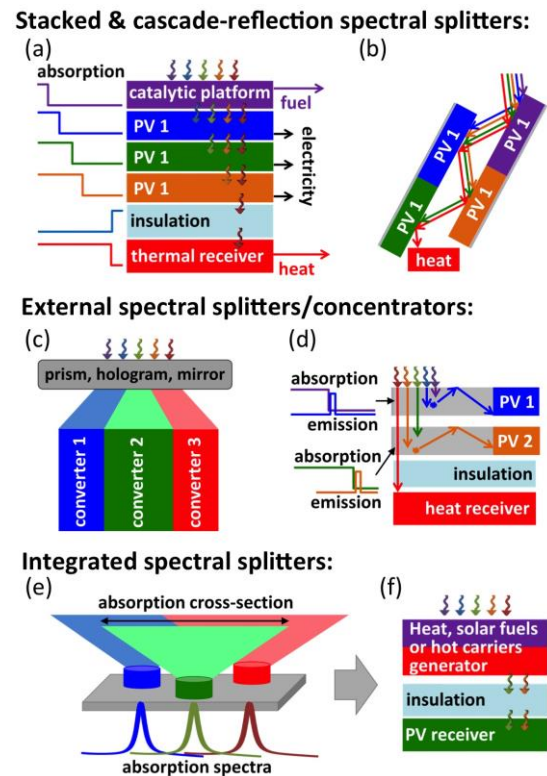

Figure 1 – Various types of spectral splitters.

achieved with planar light-guides either passively (by light trapping and guiding) or actively – by down-converting photon energy by embedded luminescent material (Fig. 1d), yet the optical efficiencies of such schemes need to be improved [see section 11].

Light conversion platforms would greatly benefit from the development of integrated elements that simultaneously provide spectral and spatial selectivity, which translates into optical concentration[5] [see section 9]. This approach is schematically illustrated in Fig. 1e, and makes use of wavelength-scale selective absorbers with large overlapping absorption cross-sections. Spectral selectivity of individual absorbers can be governed by their localized optical resonances[5,6] and/or via long-range interactions that form quasi-localized lattice modes at different wavelengths[7]. Although challenging, this scheme can be realized with resonant plasmonic and dielectric nanoantennas. Photons not captured by localized absorbers are harvested in the bottom layer. Such a scheme makes possible designing inverted stacks, with PV receivers as the bottom converter, and the top layer selectively harvesting shortest- and longest-wavelength photons, which are not efficiently converted by the PV cells (Fig. 1f).

Advances in science and technology to meet challenges – The multi-junction stacked PV is the most mature spectral-splitting technology. Despite reaching impressive 46% efficiency, it still falls below the theoretical limits (Fig. 2a)[8]. Additional external spectrum splitting elements can further improve the

efficiency of PV stacks (e.g. in UNSW cells). In turn, solar-thermal converters rely on high concentration to compensate for the radiative losses at high temperatures. This technology can significantly benefit from the development of selective absorbers[9,10], which suppress emission at longer wavelength and can operate at high temperatures [see section 17]. Absorbers with angular selectivity (i.e., those that can only absorb/emit light within a narrow angular range to match that of incoming sunlight[11]) can offer even higher efficiency (Fig. 2b). Spectral and angular selectivity can be achieved via external filters or by designing the absorber itself to be selective.

Another important issue in the solar energy conversion is the intermittent nature of the sunlight, which calls for the development of the energy storage solutions. High cost of electrical storage and a possibility of combining PV and solar-thermal engines in hybrid platforms fueled interest in the thermal storage[12]. Efficiency of the PV cells degrades if they operate at high temperature matching that of the heat receiver (Fig. 2c). This calls for the development of transparent thermal insulators and integrated spectral splitters to further boost the hybrid device efficiency. External spectrum splitting also alleviates thermal issues, and – in combination with spectral and angular selectivity of the thermal emitter – is predicted to offer promise of achieving thermal upconversion of photon energy (Fig. 2d)[13]. Another way to reduce radiative losses can be by topping thermal absorbers with transparent thermal insulators, creating non-isothermal (i.e., externally-cool internally-hot) converters[14,15].

Another type of non-isothermal converters – known as hot-carrier converters – is based on harvesting photo-excited electrons before they thermalize to the temperature of the crystal lattice [see also sections 5,9,14]. Despite high predicted efficiency limit[16], development of such converters has been stymied by the difficulties in efficient extraction of hot carriers. Not only the carriers need to be harvested within an ultra-short time period (below a picosecond), but also the efficiency of commonly used filters such as e.g. Schottky barriers is low (Fig. 2e). Furthermore, large enough population of carriers hot enough to pass through the energy filter cannot be easily created by sunlight in conventional materials such as noble metals[17]. Our calculations predict that material engineering [see sections 5-8] to tailor the electron density of states in combination with spectral splitting schemes can boost efficiency of hot carrier converters (Fig. 2e,f)[18]. Hot carrier converters that make use of plasmonic nano-elements naturally benefit from high spectral and spatial selectivity, and can make use of the integrated spectral splitting scheme shown in Fig. 1f.
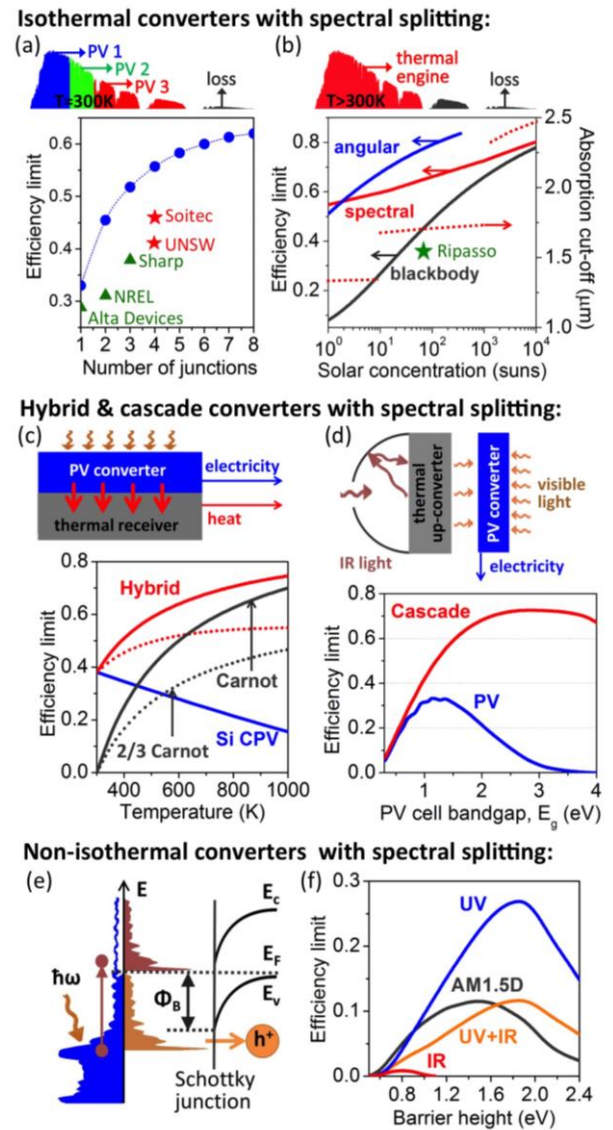

Figure 2 – Predicted and achieved efficiencies of solar conversion platforms with spectral splitting. In theoretical limits calculations, thermal engines are assumed to be operating at Carnot efficiency, and PV cells – at Shockley–Queisser efficiency; solar concentration: (a,d) 1 sun, (c,f) 100 suns.

Concluding Remarks – Spectral selectivity can be achieved by the choice of the receiver material, which calls for the development of high-quality PV materials and heat absorbers stable at high temperatures [see sections 7-9,15-17]. The use of external splitters shifts the emphasis to the design of optical elements, which ideally combine selectivity, high concentration, and low losses. Non-isothermal energy converters are promising, but call for significant advances in material design and integration. Hybrid schemes with energy storage in the form of heat or fuels are highly desirable.

References

[1] Boriskina, S. V., Tong, J. K., Ferry, V. E., Michel, J.., Kildishev, A. V., "Breaking the limits of optical energy conversion," Opt. Photonics News(July/Aug), 50–53 (2015).

[2] Mojiri, A., Taylor, R., Thomsen, E.., Rosengarten, G., "Spectral beam splitting for efficient conversion of solar energy: A review," Renew. Sustain. Energy Rev. **28**(0), 654–663 (2013).

[3] Imenes, A. G.., Mills, D. R., "Spectral beam splitting technology for increased conversion efficiency in solar concentrating systems: a review," Sol. Energy Mater. Sol. Cells **84**(1-4), 19–69 (2004).

[4] Atwater, H., Polman, A., Kosten, E., Callahan, D., Spinelli, P., Eisler, C., Escarra, M., Warmann, E.., Flowers, C., "Nanophotonic design principles for ultrahigh efficiency photovoltaics," Nobel Symp. 153 Nanoscale Energy Convert. **1519**(1), 17–21, AIP Publishing (2013).

[5] Hu, Q., Xu, D.-H., Zhou, Y., Peng, R.-W., Fan, R.-H., Fang, N. X., Wang, Q.-J., Huang, X.-R.., Wang, M., "Position-sensitive spectral splitting with a plasmonic nanowire on silicon chip.," Sci. Rep. **3**, 3095, Nature Publishing Group (2013).

[6] Boriskina, S. V., Ghasemi, H.., Chen, G., "Plasmonic materials for energy: From physics to applications," Mater. Today **16**(10), 375–386 (2013).

[7] Boriskina, S. V., Lee, S. Y. K., Amsden, J. J., Omenetto, F. G.., Dal Negro, L., "Formation of colorimetric fingerprints on nano-patterned deterministic aperiodic surfaces.," Opt. Express **18**(14), 14568–14576 (2010).

[8] Green, M. A., Emery, K., Hishikawa, Y., Warta, W.., Dunlop, E. D., "Solar cell efficiency tables (Version 45)," Prog. Photovoltaics Res. Appl. **23**(1), 1–9 (2015).

[9] Tong, J. K., Hsu, W.-C., Huang, Y., Boriskina, S. V.., Chen, G., "Thin-film 'Thermal Well' emitters and absorbers for high-efficiency thermophotovoltaics," Optics, Sci. Reports **5**, 10661 (2015).

[10] Boriskina, S. V., Tong, J. K., Hsu, W.-C., Weinstein, L., Huang, X., Loomis, J., Xu, Y.., Chen, G., "Hybrid optical-thermal devices and materials for light manipulation and radiative cooling," Proc. SPIE 9546, Act. Photonic Mater. VII, 95461U (2015).

[11] Shen, Y., Ye, D., Celanovic, I., Johnson, S. G., Joannopoulos, J. D.., Solja i, M., "Optical broadband angular selectivity," Science. **343**(6178), 1499–1501 (2014).

[12] Branz, H., "http://arpa-e.energy.gov/sites/default/files/documents/files/FOCUS_ProgramOverview.pdf."

[13] Boriskina, S. V., Chen, G., "Exceeding the solar cell Shockley-Queisser limit via thermal up-conversion of low-energy photons," Opt. Commun. **314**, 71–78 (2014).

[14] Chen, G., Wang, E. N., Boriskina, S. V., McEnaney, K., Ghasemi, H., Yerci, S., Lenert, A., Yang, S., Miljkovic, N., et al., "Internally-heated thermal and externally-cool photovoltaic cascade solar system for the full solar spectrum utilization," US 20150053266 A1 (2015).

[15] Ni, G., Miljkovic, N., Ghasemi, H., Huang, X., Boriskina, S. V., Lin, C.-T., Wang, J., Xu, Y., Rahman, M. M., et al., "Volumetric solar heating of nanofluids for direct vapor generation," Nano Energy **17**, 290–301 (2015).

[16] Ross, R. T.., Nozik, A. J., "Efficiency of hot-carrier solar energy converters," J. Appl. Phys. **53**(5), 3813, American Institute of Physics (1982).

[17] White, T. P.., Catchpole, K. R., "Plasmon-enhanced internal photoemission for photovoltaics: Theoretical efficiency limits," Appl. Phys. Lett. **101**(7), 73904–73905, AIP (2012).

[18] Boriskina, S. V., Zhou, J., Hsu, W.-C., Liao, B.., Chen, G., "Limiting efficiencies of solar energy conversion and photo-detection via internal emission of hot electrons and hot holes in gold," Proc. SPIE 9608, Infrared Remote Sens. Instrum. XXIII, 960816, SPIE (2015).

14. A path upward: new upconversion schemes for improving photovoltaics – Di M Wu, Michael D Wisser, Alberto Salleo and Jennifer Dionne

Stanford University

Status – Thermodynamic considerations limit photovoltaic efficiency to a maximum of 30% for single-junction solar cells under one-sun illumination. The Carnot limit, however, sets the maximum for terrestrial solar cell efficiencies at 95% [see sections 1,20]. To close the efficiency gap between these limits, multijunction cells [see sections 3,11], thermophotovoltaic cells [see sections 13-18], and solar concentrators [see sections 10-13] are each promising approaches. Upconversion (UC) can complement these strategies. As illustrated in Figure 1a, upconverters convert sub-band gap solar photons to above band gap photons, increasing the cell's short-circuit current. Modelling predicts that upconversion could increase the theoretical maximum efficiency of a single-junction solar cell from 30% to 44% for non-concentrated sunlight.[1] An important advantage of upconversion is electrical isolation from the active layer of the cell, eliminating the need for current- or lattice-matching.

In recent years, upconverting materials have been used to bolster the performance of photoelectrochemical cells, crystalline and amorphous silicon cells, organic cells, and dye-sensitized solar cells. [2] The record improvement was demonstrated this year with lanthanide upconversion applied to a bifacial crystalline silicon cell under 94-suns concentration, resulting in a 0.55% increase in cell efficiency. [3]

Current and Future Challenges – While the performance of solar upconverting devices has been steadily improving, a substantial gap remains between theoretical cell improvements and experimental realizations. Three major challenges include: 1) increasing the efficiency of upconversion; 2) ensuring spectral overlap with solar cells; and 3) increasing the upconverter absorption bandwidth.

The limitations on upconversion efficiency are rooted in the upconversion mechanism. Generally, upconversion of incoherent, low-power light requires a metastable intermediate state for the first excited electron to populate until a second photon is absorbed, as highlighted in yellow in Figure 1b. Two materials systems have the requisite energy levels: lanthanide ion systems and bimolecular systems. In lanthanide ions, the long-lived state is an f-orbital with parity-forbidden decay to the ground state; in bimolecular systems, it is a long-lived triplet state populated through intersystem crossing. Lanthanide upconversion is often less efficient than bimolecular upconversion in
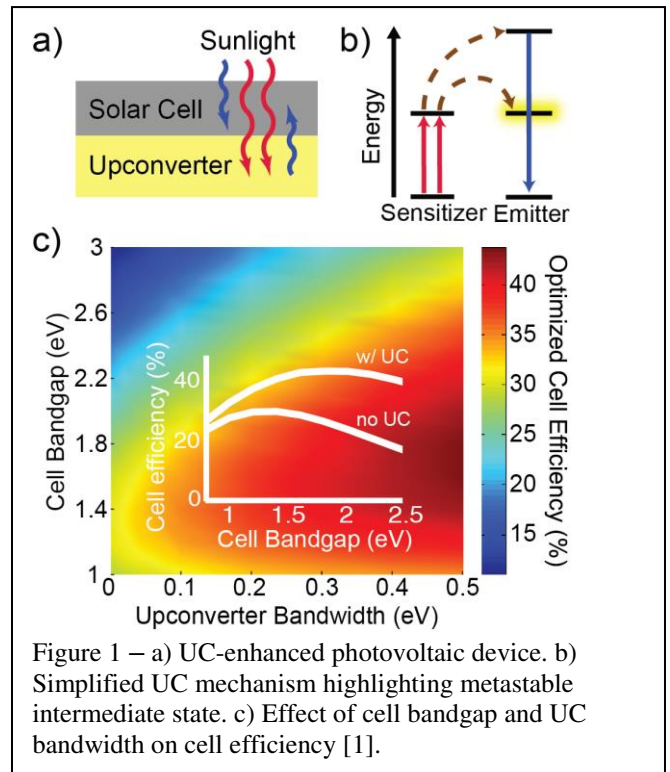

Figure 1 – a) UC-enhanced photovoltaic device. b) Simplified UC mechanism highlighting metastable intermediate state. c) Effect of cell bandgap and UC bandwidth on cell efficiency [1].

part because in the former, both absorption and emission occur between weak f-f transitions, limiting both the light absorbed and the efficiency with which it is emitted. In bimolecular upconversion, absorption and emission occur between bright singlet states and, with the proper selection of sensitizer and emitter dyes, the major bottleneck to efficiency is energy transfer between triplet states. The upconversion emission from both material systems has a quadratic dependence on incident power in low-flux illumination conditions, and efficiency typically increases with incident power density. Consequently, all demonstrations of effective upconversion-enhanced solar cells to date have been performed under laser or concentrated solar illumination.

The second challenge is tuning the spectral position of upconverter absorption and emission to make optimal use of sub-band gap light. For example, the energy levels of lanthanide ions allow absorption of low-energy light below the silicon band gap and re-emission above it, but the f-orbital energies can only be slighted tuned with the host lattice and are effectively fixed. Bimolecular upconverters have synthetically tunable absorption but often operate above the band gap of many solar cell materials. Continued exploration of infrared-absorbing triplet sensitizers will increase the relevance of these materials.

A final challenge is extending the absorption bandwidth. As shown in Figure 1c, the potential cell efficiency improvements increase with upconverter bandwidth.[1] Most studies to date have examined the performance of an individual upconverter; combining sensitizers to increase the absorption bandwidth for

both lanthanide and molecular upconverters is a direction that merits further exploration.

Advances in Science and Technology to Meet Challenges – Two approaches to addressing these challenges include: 1) improving existing lanthanide and bimolecular systems, and 2) exploring radically new upconversion schemes. Extensive investigations of the host lattice for lanthanide upconversion have yielded many key design principles, including low phonon energy, optimized interion spacing, and minimization of defects. New host lattices such as Gd_2O_2S that fulfill these requirements have demonstrated lanthanide upconversion quantum yields exceeding 15% (with a theoretical maximum of 50%).[6] While bimolecular upconversion in solids is often limited by intermolecular energy transfer, novel matrices have efficiencies approaching those in solution, with up to 17% reported in a polymer [7].

To address spectral considerations for solar energy conversion, design of new infrared absorbing supramolecular dyes and hybrid upconverter-nanoantenna materials are promising approaches. For example, adsorbing of infrared dyes to the surface of upconverting nanoparticles led to a 3300x increase in upconversion emission relative to the bare nanoparticle. [8] Plasmonic nano-antennas can increase the upconversion absorption bandwidth while also increasing the radiative rate of emission [see sections 9,13] [9].

An emerging approach that could revolutionize the efficiency and spectral tunability of upconverters is the use of hybrid semiconductor materials. Semiconductors generally absorb light with greater bandwidth than molecules or ions. Furthermore, their band gaps can be tuned with composition over the energy range most relevant for solar cells [see sections 7,8]. This tunability can be used to craft a potential energy landscape allowing sequential absorption of low-energy photons in one material followed by radiative recombination in a neighboring semiconductor.

For example, Figure 2a illustrates hot carrier upconversion in plasmonic materials interfaced with semiconductors. Here, a hot hole and a hot electron are independently created through absorption of light in a metallic nanostructure. These hot carriers are injected into a semiconductor quantum well, where they are trapped until radiatively recombining with the corresponding carrier. Judicious selection of plasmonic materials and semiconductors leads to light emitted with higher energy than that absorbed. This scheme has a theoretical upconversion efficiency of 25% using 5 nm silver nanocubes, with absorption and emission
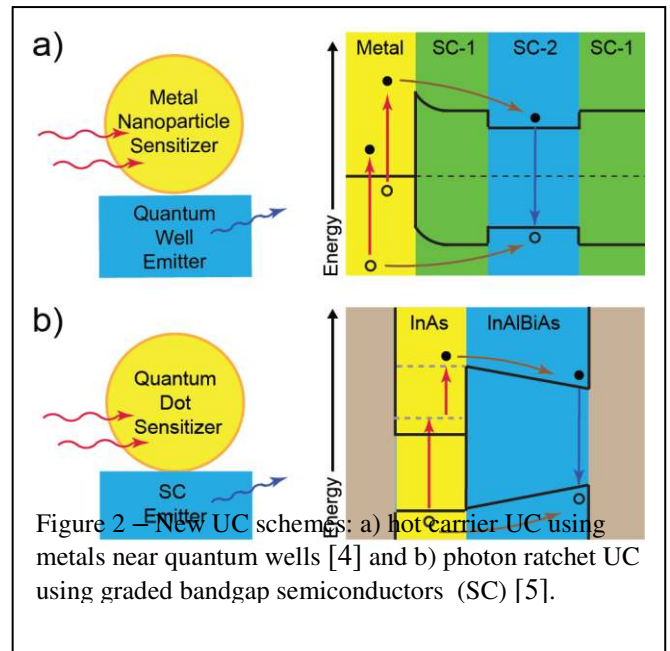

Figure 2 – New UC schemes: a) hot carrier UC using metals near quantum wells [4] and b) photon ratchet UC using graded bandgap semiconductors (SC) [5].

tunable through geometry and material [see sections 9,13] [4].

A second approach to semiconductor upconversion is shown in Figure 2b [see also sections 5,6]. Here, light absorption occurs in quantum dots with valence band edges matched to a neighboring semiconductor with a graded bandgap. After a low-energy photon is absorbed by an InAs quantum dot, exciting an electron into the conduction band, the hole is rapidly injected into the InAlBiAs layer. As in hot carrier upconversion, the energy barrier back into the InAs is high enough to prevent the reverse process, establishing a long-lived intermediate state. A second low-energy photon excites the intermediate-state electron above the conduction band edge of the neighboring material. The electron is injected into the InAlBiAs, where the hole and electron can radiatively recombine, emitting a photon of higher energy than either of those absorbed. [5]

Finally, research on triplet energy transfer between organic dyes and semiconducting nanostructures is another promising development for upconversion. For example, a recent study has shown that a semiconductor quantum dot can serve as a triplet sensitizer for dyes attached to its surface[10]. The quantum dots can absorb near-infrared light, improving spectral overlap with the needs of photovoltaics. Design of hybrid upconverters that selectively incorporate the best properties of each material is a strategy that merits further attention.

Concluding Remarks – Upconversion holds significant potential as an inexpensive and generalizable way to improve the efficiency of any solar cell. Existing upconverters, however, lack the efficiency or optimal spectral characteristics for

integration into commercial solar cells. The study of canonical upconverting materials, including lanthanide and bimolecular systems, has provided key insight into the upconversion process and the limiting factors at play. Design of radically new materials and new upconverting schemes -- including those based on semiconductors -- is rapidly moving the field forward (and upward).

References

[1] Briggs J A, Atre A C and Dionne J A 2013 Narrow-bandwidth solar upconversion: Case studies of existing systems and generalized fundamental limits *Journal of Applied Physics* **113** 124509

[2] Schulze T F and Schmidt T W 2014 Photochemical upconversion: Present status and prospects for its application to solar energy conversion *Energy Environ. Sci.*

[3] Fischer S, Favilla E, Tonelli M and Goldschmidt J C 2015 Solar Energy Materials & Solar Cells *Solar Energy Materials and Solar Cells* **136** 127–34

[4] Naik G V and Dionne J A 2015 Photon Upconversion with Hot Carriers in Plasmonic Systems *arXiv* **physics.optics** 4159

[5] Sellers D G, Polly S J, Zhong Y, Hubbard S M, Zide J M O and Doty M F New Nanostructured Materials for Efficient Photon Upconversion *IEEE J. Photovoltaics* **5** 224–8

[6] Fischer S, Martín-Rodríguez R, Fröhlich B, Krämer K W, Meijerink A and Goldschmidt J C 2014 Journal of Luminescence *Journal of Luminescence* **153** 281–7

[7] Monguzzi A, Bianchi F, Bianchi A, Mauri M, Simonutti R, Ruffo R, Tubino R and Meinardi F 2013 High Efficiency Up-Converting Single Phase Elastomers for Photon Managing Applications *Adv. Energy Mater.* n/a–n/a

[8] Zou W, Visser C, Maduro J A, Pshenichnikov M S and Hummelen J C 2012 Broadband dye-sensitized upconversion of near-infrared light *Nature Photon* **6** 560–4

[9] Wang P, Li Z, Salcedo W J, Sun Z, Huang S and Brolo A G 2015 2. Experimental section *Phys. Chem. Chem. Phys.* **17** 16170–7

[10] Huang Z, Li X, Mahboub M, Hanson K M, Nichols V M, Le H, Tang M L and Bardeen C J 2015 Hybrid Molecule–Nanocrystal Photon Upconversion Across the Visible and Near-Infrared *Nano Lett*

15. Thermophotovoltaics: an alternative strategy for converting heat to electricity –
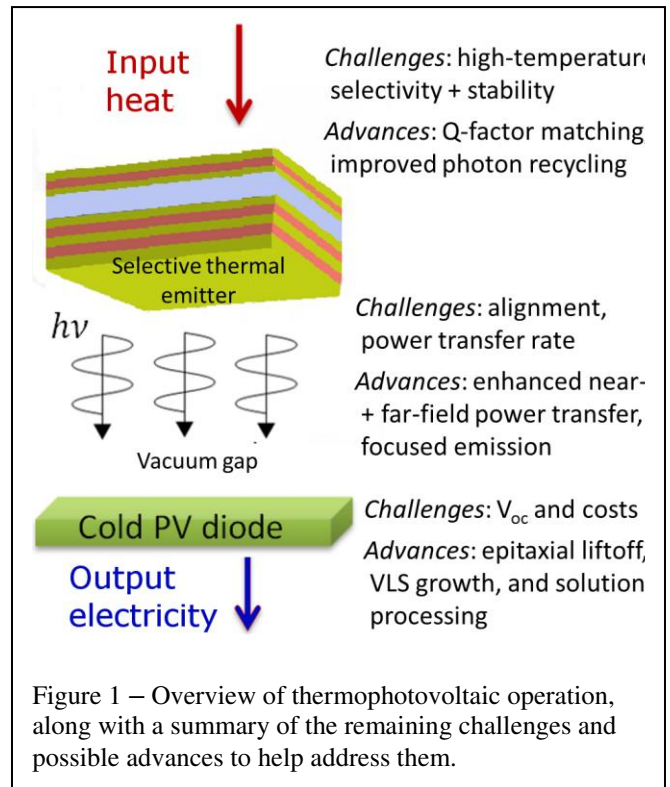
Peter Bermel
Purdue University

Status – Thermophotovoltaics (TPV) convert heat into electricity by using thermally radiated photons to illuminate a photovoltaic (PV) cell, as shown in Fig. 1 [1]. In comparison with alternative strategies for converting heat into electricity, TPV has potential for quiet, compact, reliable, and highly efficient operation, although several barriers to widespread adoption remain. The original demonstration of TPV at Lincoln Laboratories in 1956 used a camping lantern to illuminate a silicon-based "solar battery" to generate electricity [2]. However, compared to solar PV, a TPV thermal emitter is much colder, emitting predominantly in the infrared. Thus, within a decade, work began on TPV systems with smaller bandgap PV cells.

Initial work focused on germanium, but more recent work has included higher-efficiency gallium antimonide (GaSb) [3], as well as ternary and quarternary III-V materials such as InGaAs and InGaAsSb [4]. Nonetheless, the broad bandwidth of thermal radiation gives rise to a great deal of wasted mid-wavelength and long-wavelength infrared radiation [1]. To address this problem, optical short-pass filters have been placed on the front or back side of PV cells to reflect otherwise unused light back to the emitter. This approach constitutes external photon recycling, and has been demonstrated to improve overall efficiencies [4-5] [see also sections 4,13]. Combining these innovations has led to conversion efficiencies of radiated power into electricity as high as 23.6% [4].

Nonetheless, theoretical calculations have shown that there is room for a great deal of further improvement in TPV efficiencies [see also sections 16, 20]. In particular, several theoretical studies have shown that ultimate efficiencies are highly dependent on the maximum emitter temperature and emitter designs, and that in some scenarios the efficiency of the overall TPV system can exceed 50% [1], as shown in Fig. 2. By creating structures with emissivity concentrated primarily at wavelengths matching the regions of high external quantum efficiency for the PV cells utilized, selective emission can be a key driver of improved performance. Specific structures with potential for high efficiencies that have been proposed and built to date include 1D multilayer stacks [6], 2D metallic arrays of holes [7], and 3D woodpile photonic crystals [8].

Current and Future Challenges – In order for TPV to approach its theoretical limits and make the transition to a practical technology, there are a number of challenges that must first be overcome.

Figure 1 – Overview of thermophotovoltaic operation, along with a summary of the remaining challenges and possible advances to help address them.

First, it is critical to further improve the theoretical design and experimental fabrication of selective emitters to offer greater high-temperature stability and performance [see also section 17]. Many simpler emitter structures, such as metallic sheets, inevitably experience significant degradation in wavelength selectivity at high temperatures. More complex nanostructures can avoid some of these challenges, but are more vulnerable to structural degradation even at temperatures well below the bulk melting point of the underlying elements (e.g., refractory metals like tungsten).

Second, it is important to consider strategies for reducing the need for precise alignment between emitters and receivers. High-performance external photon recycling strategies in particular generally require precise alignment, yet have zero tolerance for direct mechanical contact because of the thermal gradient. This combination may be experimentally unrealistic to achieve, so more straightforward alternatives would be highly beneficial.

Third, it is crucial to achieve improved understanding of novel physical phenomena in thermal radiation, and develop appropriate strategies for harnessing them. One particular emerging topic concerns the potential to achieve thermal radiation power levels that appear to exceed the common understanding of Planck's blackbody law [see section 1], through alternative geometric surfaces with increased surface area offering improved impedance matching between high density of state materials and air [9]. Another promising approach uses sub-wavelength gaps between emitter and receiver

structures to transfer power in the near-field exceeding that of a blackbody [see section 16]. However, alignment of macroscopic plates at nanometer-scale distances without physical contacting would seem to be an even more prohibitive experimental challenge than discussed previously.

Finally, reducing the cost and improving the performance of the low-bandgap photovoltaic cells is often a challenge. Even for relatively expensive GaSb cells (E_g=0.7 eV), this difficulty manifests primarily in low open circuit voltages (typically 250 mV or less), which has follow-on effects for the fill factor and overall efficiency of the TPV system, even in the presence of an ideal thermal emitter with excellent photon recycling.

Advances in Science and Technology to Meet Challenges – To surmount the challenges discussed above, a number of promising approaches are under active investigation at this time. To improve the selectivity and thermal stability of emitters, a couple of key strategies are emerging. First, quality factor matching approaches that combine naturally selective albeit weak emitters, such as rare-earth doped crystals (e.g., erbium aluminum garnet), with photonic crystals having resonant modes at the same key wavelengths [10]. Second, next-generation photon recycling approaches that sharply reduce the "effective" emissivity observed from outside the photon recycling system. With sufficient selectivity, additional benefits can be realized, such as dielectric waveguides for increasing separation between emitters and receivers – particularly useful for maintaining large thermal gradients outside of ultra-high vacuum.

In parallel, advances are needed in terms of reliability and stability of selective thermal emitters [see section 17]. For example, work has recently been performed to fill in the voids for 2D and 3D photonic crystal structures with optically transparent diffusion barrier materials to greatly improve thermal stability. With appropriate choice of materials, transparent encapsulation can be performed to package the high-temperature emitters against softening and oxidation, which are often difficult to avoid. This also offers the possibility of heterogeneous integration with other types of structures that promote photon recycling, without mechanical failures from large thermal gradients.

In terms of realizing new physical mechanisms for TPV, one promising approach would be to develop and use angle-selective thermal emitters to more naturally concentrate light on a distant receiver, which would reduce the need for precise alignment between emitter and receiver. For near-field thermal transfer, promising alternative strategies include using an array of sharp tips (as in transmission electron microscopy) to achieve precise alignment and sufficient power transfer.

Another needed advance would be improvements in both efficiency and manufacturability for low-bandgap photovoltaic diodes. Here, several possibilities could be considered. First, epitaxial liftoff of high-quality direct bandgap III-V materials on re-usable substrates
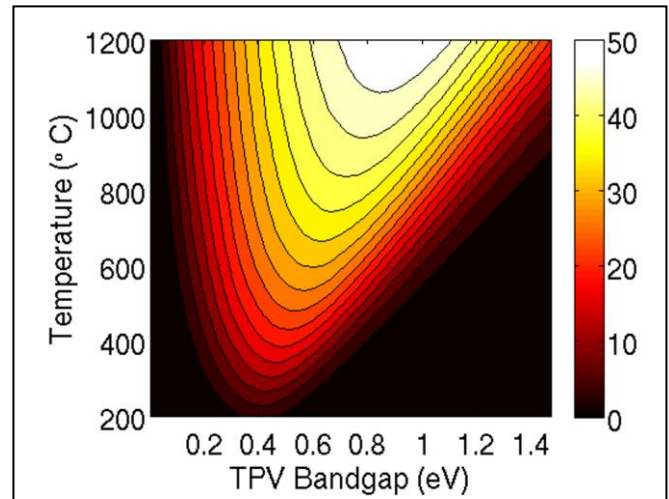

Figure 2 – Illustration of the potential of thermophotovoltaics (TPV). Using an integrated selective emitter structure can shape thermal radiation to match the PV cell bandgap. Efficiency is plotted as a function of bandgap and temperature. Maximum efficiencies may reach up to 50% for PV cell bandgaps of 0.7-1.1 eV at 1200 ºC.

could allow for record efficiencies at much more reasonable costs. Second, in situ VLS growth from metallic precursors should be considered, as recently demonstrated for indium phosphide photovoltaics. Third, solution-processed low bandgap materials could be used in TPV, such as perovskites for photovoltaics.

Concluding Remarks – In conclusion, thermophotovoltaics is a technology that has the proven capability of quietly converting heat into electricity without moving parts [1]. The best designs to date have combined high-temperature operation, high-performance InGaAs PV cells, and long-pass filters to achieve up to 23.6% conversion of thermal radiation into electricity [4]. TPV also has the potential for even higher performance in the future, potentially exceeding 50% [1], as shown in Fig. 2 [see also sections 13,16], as well as lower costs. Achievement of such metrics could be enabled by future advances in selective emitter or photovoltaic technology, which may include the exploration of novel materials, as well as the incorporation of novel physical phenomena, such as enhanced out-coupling for thermal emitters in the near or far fields, as summarized in Fig. 1.

References

[1] Peter Bermel, Michael Ghebrebrhan, Walker Chan, Yi Xiang Yeng, Mohammad Araghchini, Rafif Hamam, Christopher H. Marton, Klavs F. Jensen, Marin Soljacic, John D. Joannopoulos, Steven G. Johnson, Ivan Celanovic, "Design and global optimization of high-efficiency thermophotovoltaic systems", Opt. Express 18, A314-A334 (2010).

[2] H. H. Kolm, "Solar-battery power source," Tech. rep., MIT Lincoln Laboratory (1956). Quarterly Progress Report, Group 35, p. 13.

[3] Fraas, Lewis, Russ Ballantyne, She Hui, Shi-Zhong Ye, Sean Gregory, Jason Keyes, James Avery, David Lamson, and Bert Daniels. "Commercial GaSb cell and circuit development for the midnight sun® TPV stove." In Fourth NREL conference on thermophotovoltaic generation of electricity, vol. 460, no. 1, pp. 480-487. AIP Publishing, 1999.

[4] Wanlass, M. W., S. P. Ahrenkiel, R. K. Ahrenkiel, J. J. Carapella, R. J. Wehrer, and B. Wernsman. "Recent Advances in Low-Bandgap, InP-Based GaInAs/InAsP Materials and Devices for Thermophotovoltaic (TPV) Energy Conversion." In THERMOPHOTOVOLTAIC GENERATION OF ELECTRICITY: Sixth Conference on Thermophotovoltaic Generation of Electricity: TPV6, vol. 738, no. 1, pp. 427-435. AIP Publishing, 2004.

[5] F. O'Sullivan, I. Celanovic, N. Jovanovic, J. Kassakian, S. Akiyama, and K. Wada, "Optical characteristics of 1D Si/SiO2 photonic crystals for thermophotovoltaic applications," J. Appl. Phys. 97, 033,529 (2005).

[6] Walker R. Chan, Peter Bermel, Robert C.N. Pilawa-Podgurski, Christopher H. Marton, Klavs F. Jensen, Jay J. Senkevich, John D. Joannopoulos, Marin Soljacic, and Ivan Celanovic, "Toward high-energy-density, high-efficiency, and moderate-temperature chip-scale thermophotovoltaics," Proc. Natl. Acad. Sci. 110, 5309–5314 (2013).

[7] Zhiguang Zhou, Qingshuang Chen, Peter Bermel, "Prospects for high-performance thermophotovoltaic conversion efficiencies exceeeding the Shockley-Queisser limit," Energy Conversion and Management 97, 63-69 (2015).

[8] J. M. Gee, J. B. Moreno, S.-Y. Lin, and J. G. Fleming, "Selective emitters using photonic crystals for thermophotovoltaic energy conversion," in Twenty-ninth IEEE Photovolt. Spec. Conf. (2002).

[9] Yu, Zongfu, Nicholas P. Sergeant, Torbjørn Skauli, Gang Zhang, Hailiang Wang, and Shanhui Fan. "Enhancing far-field thermal emission with thermal extraction." Nature communications 4 (2013): 1730.

[10] Enas Sakr, Zhiguang Zhou, and Peter Bermel, "High Efficiency Rare-Earth Emitter for Thermophotovoltaic Applications," Applied Physics Letters 105, 111107 (2014).

16. Near-field radiative transfer in the energy conversion schemes – Jean-Jacques Greffet

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Status – The field of radiative heat transfer at the nanoscale started with the experimental observation [1] that the flux exchanged between two metallic plates separated by a submicron gap d could be larger than the Stefan-Boltzmann law. We now have a simple picture that explains the reason for this extraordinary flux [2] as depicted in figure 1. The radiative flux is given by the sum of the intensity over all angles from normal incidence to grazing incidence. Let us instead adopt an electromagnetic point of view and sum over all parallel wavevectors of the electromagnetic fields in the (k_x, k_y) plane. For parallel wavevectors with a modulus $k_p < \omega/c$, where ω is the frequency and c is the light velocity, the waves are propagating (Fig. 2 b) and there is no difference with summing over all angles.

The additional heat flux can be partly attributed to additional modes which are propagating in the medium but not in the air with k_p in the range $[\omega/c, n\omega/c]$ producing the so-called frustrated total internal reflection (Fig. 2 c). A more complete theoretical explanation provided by Polder and van Hove [3] clarified the role of the evanescent modes with arbitrary large wavevectors (Fig. 2d) [see also section 1]. The transmission factor associated to each mode decays exponentially as $\exp(-k_p d)$ and introduces a cutoff: only modes with $k_p < 1/d$ contribute to the heat flux. Hence, the heat flow increases as $1/d^2$ because the number of modes increases as the area of the disk limited by $k_x^2 + k_y^2 = 1/d^2$.

Experimental observation of this enhanced flux appeared to be extremely difficult at ambient temperatures [4] so that this effect remained a physics peculiarity until it was discovered [5] that the heat flux can be much larger for dielectrics than for metals. This is due to the fact that the transmission factor associated to each mode is very low for metals but close to 1 for dielectrics at a particular frequency in the infrared, due the resonant excitation of gap modes produced by surface phonon polaritons. It follows that *the flux is quasi monochromatic*. Large heat fluxes have been observed [6,7] confirming theoretical predictions. As shown in Fig. 1 e, *the flux is expected to be orders of magnitude larger than in the far field* so that there is a potential gain for energy conversion devices.

Current and Future Challenges – How can we take advantage of this extraordinary large and quasi monochromatic heat flux for energy conversion? In what follows, we restrict the discussion to near-field thermophotovoltaics which has been proposed as a
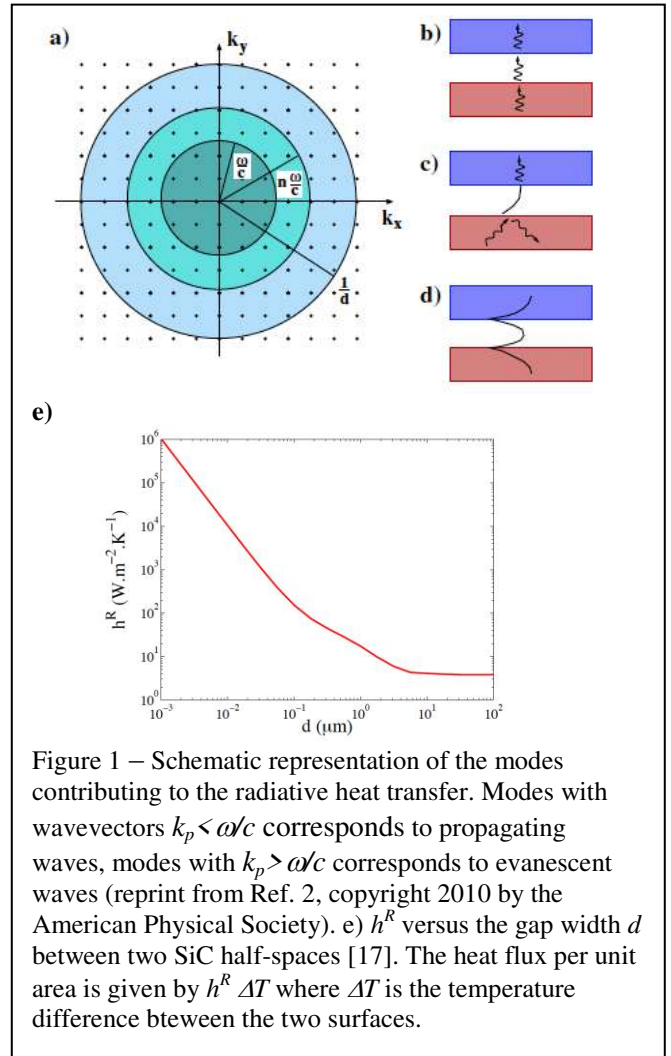

Figure 1 – Schematic representation of the modes contributing to the radiative heat transfer. Modes with wavevectors $k_p < \omega/c$ corresponds to propagating waves, modes with $k_p > \omega/c$ corresponds to evanescent waves (reprint from Ref. 2, copyright 2010 by the American Physical Society). e) h^R versus the gap width d between two SiC half-spaces [17]. The heat flux per unit area is given by $h^R \Delta T$ where ΔT is the temperature difference bteween the two surfaces.

possible candidate [5,8,9] [see also section 15]. Single junction photovoltaic cells have an efficiency limited by the so-called Shockley-Queisser limit. The key issue is the mismatch between the narrow absorption spectrum of a single junction photovoltaic cell and the broad incident spectrum of a blackbody: either the sun or a secondary source at lower temperature. Hence, infrared photons with $h\nu < E_g$ are not absorbed while photons with $h\nu > E_g$ lead to a loss of energy $h\nu - E_g$. Thermophotovoltaics is a concept that has been proposed to circumvent this limit. It amounts to illuminate the cell through a filter so that only energy at the right frequency is used, the rest being recycled in an isolated system.

Working with a *near-field thermophotovoltaic* system would have two key advantages: i) the flux is increased by several orders of magnitude as compared to the far-field case so that the output power would be dramatically increased; ii) the near-field thermal radiation can be quasi-monochromatic so that the efficiency could be above the Shockley-Queisser limit. Furthermore, increasing the current in a junction results in a larger open circuit voltage so that the output electrical power is further increased.

Alternatively, the larger flux for a given temperature difference may be a way to use energy from low temperature sources, the so-called waste heat issue. Hence, near-field thermo-photovoltaics appears as a promising option [8-13]. What are the key challenges to fully benefit from the physics of near-field heat transfer? Fabrication and thermal management raises serious difficulties as the cell needs to remain at ambient temperature while being at a distance of around 100 nm from a hot surface. The second key issue is the design of a quasi-monochromatic source at a frequency matching the cell band gap [see sections 15-17].

Advances in Science and Technology to Meet Challenges – The heat flux has been measured in the nanometric range [6, 7] between a sphere and a plane. Fabricating a system with two planar surfaces separated by a submicron distance is a challenge. The feasibility of a planar system has been demonstrated in the micron size regime by the company MTPV [10]. In this range, the gain in flux is limited to one order of magnitude and there is almost no benefit regarding the efficiency. The design and modelling of thermal management of the system will play a critical role in the final performance of the system [11].

An important feature of the near-field thermophotovoltaic cell is its potential to generate quasi-monochromatic fluxes and therefore to increase the efficiency [12]. It has been shown that an ideal surface wave resonance producing a quasi-monochromatic flux could generate efficiencies on the order of 35%. Yet, this would be obtained at unrealistically small distances on the order of less than 10 nm. In addition, there is no obvious material providing a phonon resonance at the required frequency. Using a quasi-monochromatic emitter is not necessarily the best option. Finding the best near-field emitter is an open question. It could be either a new material or a metasurface with appropriate engineered resonances. This issue is all the more challenging as the system needs to operate reliably over a long time at temperatures above 1000 K.

Another challenge is related to the development of the photovoltaic cell. As the flux is due to evanescent waves, the absorption takes place very close to the surface. As a rule of thumb, if the gap has a width d, then the absorption takes place within a distance d of the interface. In other words, the cell is very sensitive to surface defects and electron-hole recombination processes taking place close to the interface [13]. This calls for the development of efficient surface passivation processes. Optimizing the detector is also an open question. It has been suggested recently to use graphene to tailor the detector[14,15] or the flux[16].

Concluding Remarks – Radiative heat transfer can be increased by orders of magnitude in the near field. It also provides the opportunity to tailor the spectrum
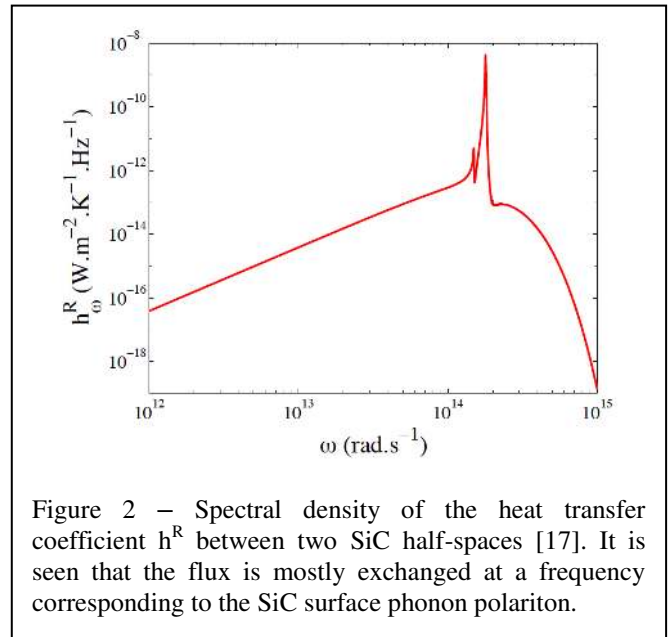

Figure 2 – Spectral density of the heat transfer coefficient h^R between two SiC half-spaces [17]. It is seen that the flux is mostly exchanged at a frequency corresponding to the SiC surface phonon polariton.

with potential benefit for the energy conversion efficiency. A near-field thermophotovoltaic energy converter could be extremly compact and could operate at relatively low temperatures offering new avenues to harvest waste heat. Yet, designing a practical device raises a number of challenges. Many groups have now reported experimental measurements of the flux in the near field with different geometries. The challenge is now to move on to design practical devices operating with gaps on the order of 100 nm in order to take full advantage of the potential.

References
[1] C.M. Hargreaves, Phys. Letters **30**A, 491 (1969)
[2] SA Biehs, E Rousseau, JJ Greffet, Phys.Rev.Lett. **105**, 234301 (2010)
[3] Polder D., van Hove M., Phys.Rev.B **4**, 3303 (1971)
[4] J.B. Xu et al., J. Appl.Phys. **76**, p7209 (1994)
[5] J.P.Mulet et al., Microscale Thermophysical Engineering **6**, 209 (2002)
[6] S. Shen et al., Nano Letters **9**, 2909 (2009)
[7] E. Rousseau, Nature Photonics **3**, 514 (2009)
[8] R.S.DiMatteo et al., Appl.Phys.Lett. **79**, 1894 (2001)
[9] A.Narayanaswamy and G. Chen, Appl.Phys.Lett. **82**, 3544 (2003)
[10] R.DiMatteo, AIP Conference Proceedings 738 p 42 (2004)
[11] M. Francoeur et al. IEEE Transactions on Energy Conversion **26**, 686 (2011)
[12] M. Laroche et al., J. Appl.Phys.**100**, 063104 (2006)
[13] K. Park et al., JQSRT 109, 305 (2008)
[14] O. Ilic et al., Opt.Express 20, 366 (2012)
[15] V.B. Svetovoy, G. Palantzas, Phys.Rev.Applied **2**, 034006 (2014)
[16] R. Messina et al., Phys.Rev.Lett.109, 244302 (2012)

[17] Jean-Philippe Mulet, Ecole Centrale Paris, 2003. Thesis title: Modélisation du rayonnement thermique par une approche électromagnétique.

17. High-temperature nanophotonics: from theory to real devices and systems – Ivan Celanovic and Marin Soljacic
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Status – While tailoring optical properties of solid state materials at room and cryogenic temperatures have been the focus of extensive research [see sections 5-8], tailoring optical properties of materials at very-high temperatures is still a nascent field. Being able to engineer optical properties, beyond what naturally occurring materials exhibit and maintaining these properties over high temperatures and over device lifecycle, has the promise to profoundly influence many fields of energy conversion, i.e., solar-thermal, thermophotovoltaics (TPV), radioisotope TPV, IR sources, incandescent light sources [1,2,3]. Indeed, the opportunities for game changing applications that would benefit immensely from high-temperature nanophotonic materials are vast, yet challenges remain formidable [see also sections 13,15,16].

In general, high temperature nanophotonic structures enable us to control and tailor spontaneous emission by virtue of controlling the photonic density of states [see section 1]. These structures enable engineering spectral and/or directional thermal emission/absorption properties, where it appears that current state of the art materials exhibit better control over spectral than directional properties. Indeed, the importance of tailoring both spectral and directional emission properties can be understood through the lens of specific applications.

Thermophotovoltaics energy conversion devices require spectrally broadband, yet omnidirectional, thermal emission (usually 1-2.5 um) with sharp cutoff corresponding to the bandgap of the photovoltaic diode [2]. Solar absorbers, for solar thermal and solar-thermophotovoltaics (STPV), need high-absorptivity over solar broadband spectrum but only within a very confined spatial angle [3,4,5]. Furthermore, many infrared sources require both spectrally and angularly confined thermal emission properties [6] [see also sections 13,15].

Current and Future Challenges – Numerous challenges arise when trying to design nanophotonic materials with precisely tailored optical properties that can operate at high temperatures (>1,100 K) over extended periods of time including the thermal cycling such as TPV portable generators, shown in Figure 1, and STPV shown in Figure 2 and Figure 3. These challenges can broadly be categorized in two groups: material selection and fabrication challenges, and design and optimization challenges (given the performance and operating conditions constraints). Material selection and fabrication challenges include

proper material selection and purity requirements to prevent melting, evaporation, or chemical reactions; severe minimization of any material interfaces to prevent thermomechanical problems such as delamination; robust performance in the presence of surface diffusion; and long-range geometric precision over large areas with severe minimization of very small feature sizes to maintain structural stability. Indeed, there is a body of work that approached the design of high-T nanophotonics.

Two types of materials are most often considered for high-temperature nanophotonics, namely refractory metals and dielectrics. Refractory metals have extremely high melting temperature and are hence stable at high temperatures. The down side of these materials is that they tend to chemically react with oxygen and other elements (i.e. carbon) at high temperatures. However, they have a relatively high reflectivity in deep IR making them amenable for 2D and 3D photonic crystal selective emitters. Dielectrics, such as SiO_2, HfO_2 are often considered for dielectric and metalo-dielectric PhCs since they tend to be less reactive at high temperatures and are also standard microfabrication materials. Interface minimization is
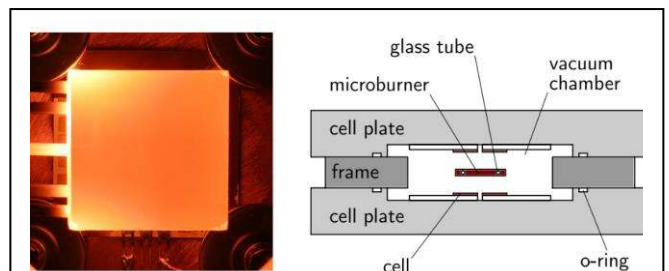

Figure 1– Micro-thermophotovoltaic MIT generator prototype; left: image of 2x2cm reactor during operation, b) cross sectional drawing of prototype system.
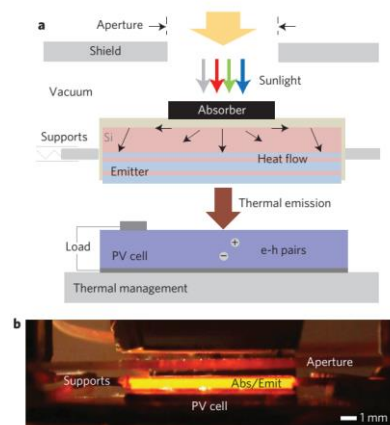

Figure 2 – Operating principle and components of the STPV. Sunlight is converted into useful thermal emission and, ultimately, electrical power, via a hot absorber–emitter. Schematic (a) and optical image (b) of our vacuum-enclosed devices composed of an aperture/radiation-shield, an array of MWNTs as the absorber, a 1D PhC, a 0.55 eV-bandgap photovoltaic cell (adopted from [5]).

another aspect of design that has to be taken into account due to thermally induced stresses and potential reactions and inter diffusion. Hence, the simpler the interfaces the better. Surface diffusion is especially pronounced for metallic PhC, 2D and 3D due to relatively high diffusion constants which tend to drive diffusion around sharp features hence degrading optical performance. Finally, nano- and micro-fabricating structures that maintain long-range geometric precision and geometrical parameters at high-T remains both a fabrication and design constraint and challenge.

Advances in Science and Technology to Meet Challenges – Two key opportunities towards practical high-temperature nanophotonic devices remain: new and more robust material systems and fabrication processes; and even higher level of control of directional and spectral properties (i.e. even more selective emission/absorption, both spectrally and directionally). In terms of materials and fabrication challenges: demonstrating high-T photonic devices with tens of thousands of hours operational stability at temperatures above 1000K; mastering materials and fabrication processes to fabricate metalo-dielectric photonic structures; developing passivation and coatings for refractory metallic structures that will be oxidatively and chemically stable in non-inert environments.

In terms of achieving the next level of control of directional and spectral properties several key challenges remain: angularly selective-broadband absorbers; spectrally highly selective broadband wide angle emitters, and spectrally highly selective broadband narrow band emitters, and near-field highly resonant energy transfer.

Concluding Remarks – The main driver for high performance high-temperature nanophotonic materials are energy conversion applications such as: solar-thermal, thermophotovoltaics, radioisotope TPV, IR and incandescent light sources. These applications would benefit greatly from robust and high performance high-T nanophotonic materials. Indeed, more work is needed that is strongly grounded in the experimental and application world. Real life constraints need to be brought into the design process in order to inform the theoretical and exploratory work. In the end, fresh and innovative thinking in terms of new theoretical approaches is always critical and it drives the field forward. However, in needs to be well targeted and directly coupled to experimental and application work to provide rapid evaluation of advanced concepts and ideas.

References
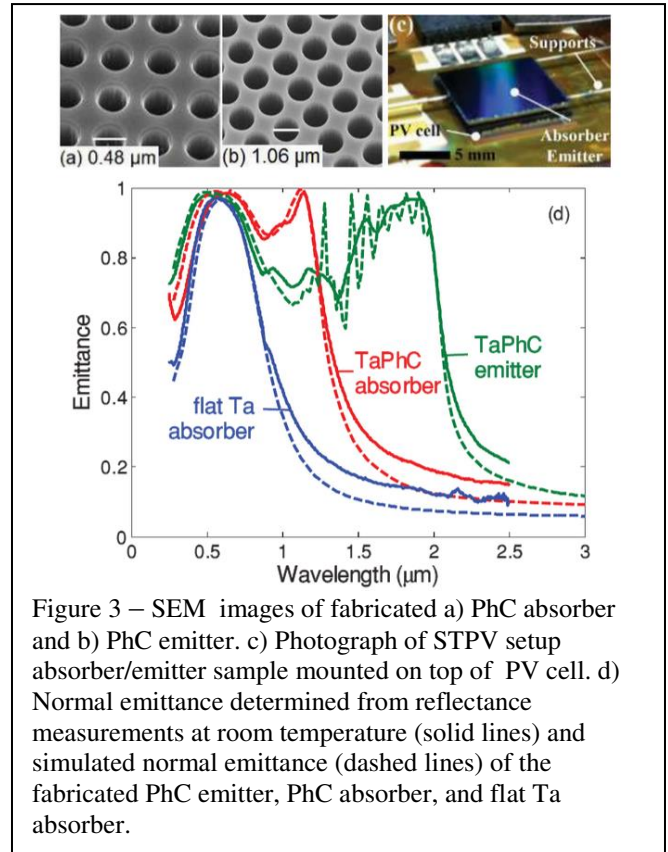
Figure 3 – SEM images of fabricated a) PhC absorber and b) PhC emitter. c) Photograph of STPV setup absorber/emitter sample mounted on top of PV cell. d) Normal emittance determined from reflectance measurements at room temperature (solid lines) and simulated normal emittance (dashed lines) of the fabricated PhC emitter, PhC absorber, and flat Ta absorber.

[1] J.G. Fleming, S. Y. Lin, I. El-Kady, R. Biswas and K.M. Ho, "All-metallic 3D photonic crystals with a large photonic band-gap" *Nature* 417, 52-55 (2002).

[2] W. R. Chan, P. Bermel, J. Senkevich, M. Ghebrebrhan, Y. X. Yeng, C. H. Marton, K. F. Jensen, S. G. Johnson, J. D. Joannopoulos, M. Soljacic, I. Celanovic, "High energy density, high efficiency, moderate-temperature chip-scale thermophotovoltaics," *Proceedings of the National Academy of Sciences*, vol.110, no.14, pp. 5309 5314, 2013.

[3] V. Rinnerbauer, S. Ndao, Y. X. Yeng, W. R. Chan, P. Bermel, J. Senkevich, J. D. Joannopoulos, M. Soljacic and I. Celanovic, "Recent developments in high-temperature photonic crystals" *Energy Environ. Sci.*, 5 (10), pp. 8815 - 8823, 2012.

[4] Y. Shen, D. Ye, I. Celanovic, S. G Johnson, J. D. Joannopoulos, M. Soljacic, "Optical Broadband Angular Selectivity," *Science*, Vol.343, p.1499 (2014).

[5] A. Lenert, D. M. Bierman, Y. Nam, W. R. Chan, I. Celanovic, M. Soljacic and E. N. Wang, "Nanophotonic Solar Thermophotovoltaics for High-performance Solar Power Generation," Nature Nanotechnologies, vol. 9, pp. 126-130, 2014

[6] Zoysa, M. D. et al. Conversion of broadband to narrowband thermal emission through energy recycling. Nature Photon. 6, 535–539 (2012).

18. Endothermic-photoluminescence: optical heat-pump for next generation PV –

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Status – Single-junction photovoltaic **(PV)** cells are constrained by the fundamental Shockley-Queisser (SQ) efficiency limit of 30%-40% **[1]** [see section 1]. This limit is, to a great extent, due to the inherent heat dissipation accompanying the quantum process of electro-chemical potential generation. Concepts such as solar thermo-photovoltaics **[2,3]** (STPV) aim to harness these thermal losses by heating a selective absorber with solar irradiation and coupling the absorber's thermal emission to a low bandgap PV cell [see sections 13-17]. Although in theory such devices can exceed 70% efficiency **[4]**, thus far no demonstration above the SQ limit was reported. This is mainly due to the requirement to operate at very high temperatures.
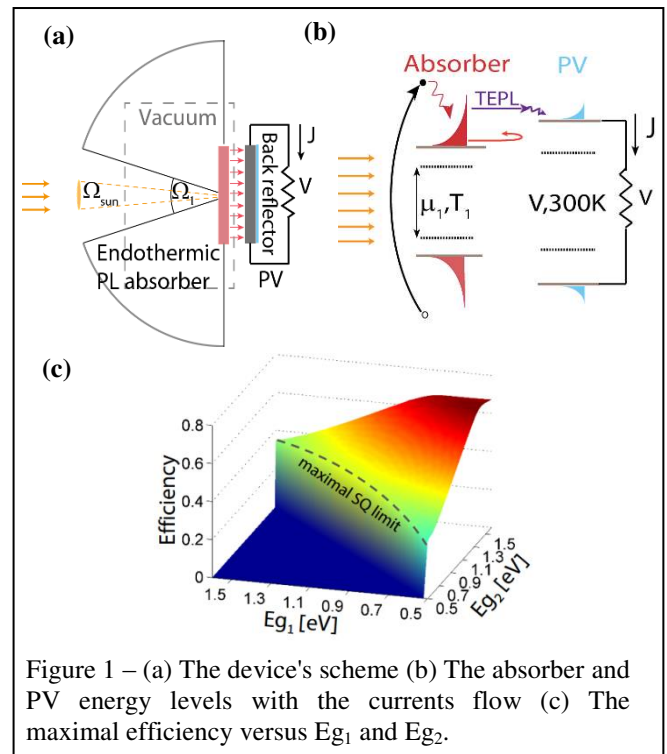
In contrast to thermal emission, photoluminescence (PL) is a non-equilibrium process characterized by a non-zero chemical potential, which defines an enhanced and conserved emission rate **[5]** [see section 1. Recently, the characteristic of PL as an optical heat pump at high temperatures was theoretically and experimentally demonstrated **[6]**. In these experiments, PL was shown to be able to extract thermal energy with minimal entropy generation by thermally induced blue-shift of a conserved PL rate.

Here we briefly introduce and thermodynamically analyze a novel thermally-enhanced-PL (TEPL) device, for the conversion of solar energy beyond the SQ limit at moderate operating temperatures. In such a device, high solar photon current is absorbed by a low bandgap thermally insulated PL-material placed in a photon-recycling cavity. Due to the rise in its temperature, the blue-shifted PL generates energetic photons in rates that are orders of magnitude higher than thermal emission at the same temperature. The PL is harvested by a high-bandgap PV cell, yielding enhanced voltage and efficiency (see detailed description below).

In addition, we present proof-of-concept experiments for TEPL operating at a narrow spectral range, where sub bandgap photons are harvested by a GaAs solar cell. Future challenges in this new direction include: **i.** Material research [see sections 5-8] for expending the overlap between the absorption line-shape and solar spectrum while maintaining high QE. **ii.** Optimizing the bandgaps with respect to the absorbed spectrum and operating temperature. **iii.** Optimizing the photon recycling efficiency [see sections 4,15]. **iv.** Exploring the fundamentals of endothermic-PL. The low operating temperatures associated with the minimal

entropy generation together with overcoming future challenges may open the way for practical realization of high efficiency next generation PV.

Current and Future Challenges – Figure 1a depicts the conceptual design of the TEPL based solar energy converter. A thermally-insulated low-bandgap PL absorber completely absorbs the solar spectrum above its bandgap and emits TEPL towards a higher bandgap PV cell, maintained at room temperature. Such a device benefits from both the high photon current of the low-bandgap absorber, and the high PV voltage.

Figure 1 – (a) The device's scheme (b) The absorber and PV energy levels with the currents flow (c) The maximal efficiency versus Eg_1 and Eg_2.

For minimizing radiation losses, a semi-ellipsoidal reflective dome recycles photons by reflecting emission at angles larger than the solid angle Ω_1 **[7]**. In addition, the PV's back-reflector **[8]** reflects sub-bandgap photons to the absorber. Figure 1b shows the absorber and PV energy levels, where μ_1 and T_1 define the absorber's thermodynamic state and its emission. In the detailed analysis of such a device, the PL absorber satisfies the balance of both energy and photon rates between the incoming and the outgoing radiation currents, while the PV satisfies only the rate balance due to the dissipated thermal energy required to maintain it at room temperature. By setting the PV's voltage, we solve the detailed balance and find the thermodynamic properties T and μ, as well as the system's *I-V* curve and its conversion efficiency [see section 1]. The analysis for various absorber and PV bandgap configurations shows maximal theoretical conversion efficiency limit of 70% for bandgap values of 0.5eV and 1.4eV, under ideal conditions of photon recycling and thermal insulation (Fig. 1c). More importantly, the expected operating temperatures at

such ideal conditions are below 1000°C, about half of the equivalent temperature required in STPV.

When approaching the experimental proof-of-concept we need to address the challenges of realizing a TEPL based solar converter. First, high quantum efficiency (QE) must be maintained at high temperatures. This limits the use of semiconductors due to non-radiative recombination mechanisms, which reduces QE with temperature. In contrast, rare-earth emitters such as Neodymium and Ytterbium are known to maintain their QE at high temperature as their electrons are localized and insulated from interactions [9]. Although their superior QE, the use of rare-earths as PL absorbers raises another challenge: the poor overlap between the solar spectrum and their absorption line-shape. Within these limits, as a proof-of-concept for the ability to harvest sub-bandgap photons in TEPL device, we experiment with $Nd^{3+}:SiO_2$ absorber coupled to a GaAs PV. The sample is placed in vacuum conditions (10^{-4} mbar), pumped by 914nm (1.35eV) laser. This pump is sub-bandgap with respect to the GaAs solar cell (1.44 eV). At room temperature the 914nm induces a PL spectrum between 905nm and 950nm. The temperature doesn't rise since each emitted photon carries similar energy to the pump photons. An additional 532nm pump, which matches the Nd^{3+} absorption line, is used to mimic an average solar photon, in order to increase both temperature and PL photon rate. The first experiment is done only with the 532nm pump in order to measure the pump power that is required for a significant blue-shift. Figure 2a shows the PL spectrum evolution with the absorbed pump intensity, indicated in suns (1sun=1000 W/m^2).

Figure 2. (a) PL evolution with pump power. (b) PV current versus time.

At pump power of 400 suns, the PL exhibits a significant blue-shifting from 905 nm to 820nm, which can be harvested by the GaAs PV. Figure 2b shows the time-dependence of the PV current under dual pump lasers. At first, an increase in current is observed when only the 914nm pump is switched on, as a result of room-temperature blue-shift (red line at *t=5*). Then, the 532nm pump is switched-on (red line at *t=10*) and the current gradually rises due to the rise in temperature. When the sample reaches 620K, the 532nm pump is switched off, leaving only the 914nm pump. The current then drops to a level two times higher than its initial value at *t=5*. This demonstrates how the heat generated in the thermalization of the 532nm pump is harvested by blue-shifting of 914nm sub bandgap photons. The green line shows the PV's current time dependence when only the 532nm pump is on, with insignificant thermal current when both pumps are off.

Advances in Science and Technology to Meet Challenges – Future demonstration of efficient TEPL conversion device requires advances in material science, development of tailored optics, and in understanding the fundamentals of PL. The presented proof-of-concept demonstrates the ability to harvest sub-bandgap photons in TEPL, yet this demonstration can operate only at narrow spectral range due to the typical absorption lines of rare-earths. The challenge of expending the absorption spectrum while maintaining high QE requires the use of laser technology knowhow, where a broad incoherent pump is coupled to a narrow emitter with minimal reduction in QE. Such sensitization may include the development of cascaded energy transfer [10] between rare-earths and transition metals. Another challenge is replacing the Nd^{3+} absorber with a lower energy gap material, for enhancing photon rate and overall efficiency. In addition to the material research, realization of an efficient device also requires the development of high quality photon recycling capabilities. This includes clever optical engineering with tailored narrow band-pass filters and cavity structure. Finally, focusing on the fundamental science, our experiments on endothermic-PL [6] show a discontinuity in the entropy and chemical potential at a critical temperature where the PL abruptly becomes thermal emission. It is fascinating to explore the thermodynamic properties of this discontinuity.

Concluding Remarks – Based on our recent experimental observations showing that photoluminescence at high temperatures is an efficient optical heat pump, we propose and analyze a solar energy converter based on TEPL. In addition, we experimentally demonstrate the TEPL's ability to harvest sub-bandgap radiation. Finally, the roadmap for achieving efficiency in such devices is detailed. We
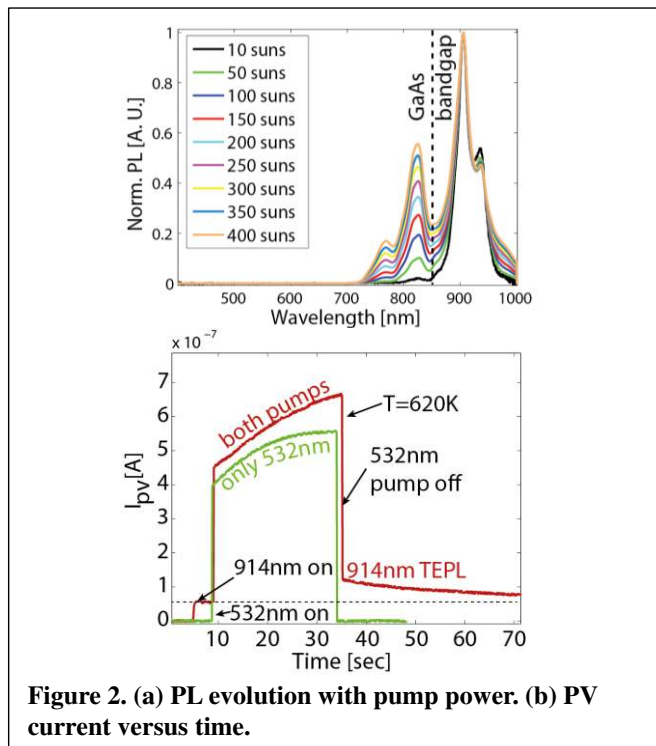
describe the expected challenges in material research, optical architecture and fundamental science. We believe that successfully overcoming these challenges will open the way for disruptive technology in PVs.

References

[1] W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells," J. Appl. Phys. **32**, 510 (1961).

[2] P. Wurfel and W. Ruppel, "Upper limit of thermophotovoltaic solar-energy conversion," IEEE Trans. Electron Devices **27**, 745–750 (1980).

[3] R. M. Swanson, "A proposed thermophotovoltaic solar energy conversion system," IEEE Proc. **67**, 446 (1979).

[4] P. Würfel, *Physics of Solar Cells: From Principles to New Concepts* (Wiley, 2008).

[5] P. Wurfel, "The chemical potential of radiation," J. Phys. C Solid State Phys. **15**, 3967–3985 (1982).

[6] A. Manor, L. L. Martin, and C. Rotschild, "On the conservation of photon rate in endothermic-photoluminescence and its transition to thermal emission," Accepted for publication in *Optica* (2015).

[7] A. Braun, E. A. Katz, D. Feuermann, B. M. Kayes, and J. M. Gordon, "Photovoltaic performance enhancement by external recycling of photon emission," Energy Environ. Sci. **6**, 1499–1503 (2013).

[8] E. Yablonovitch, O. D. Miller, and S. R. Kurtz, "The opto-electronic physics that broke the efficiency limit in solar cells," in *2012 38th IEEE Photovoltaic Specialists Conference (PVSC)* (2012).

[9] G. Torsello, M. Lomascolo, A. Licciulli, D. Diso, S. Tundo, and M. Mazzer, "The origin of highly efficient selective emission in rare-earth oxides for thermophotovoltaic applications," Nat. Mater. **3**, 632–637 (2004).

[10] C. Rotschild, M. Tomes, H. Mendoza, T. L. Andrew, T. M. Swager, T. Carmon, and M. A. Baldo, "Cascaded Energy Transfer for Efficient Broad-Band Pumping of High-Quality, Micro-Lasers," Adv. Mater. **23**, 3057–3060 (2011).

19. Harnessing the coldness of the universe by radiative cooling to improve energy efficiency and generation – Aaswath Raman, Linxiao Zhu and Shanhui Fan
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Status – With the rise of photovoltaics we have made significant progress in exploiting a powerful and renewable source of thermodynamic heat, the Sun [see sections 2-14]. However, our society has thus far largely ignored another ubiquitous resource that is equally important from a thermodynamic, and energy conversion, point of view: the cold darkness of the universe. Exploiting and harnessing this resource represents an important frontier for both energy and photonics research in the coming decade, with the potential to dramatically improve the efficiency of any existing energy conversion process on Earth.

This resource can be accessed due to a feature of Earth's atmosphere: between 8 and 13 micrometers it can be transparent to electromagnetic waves. Thus a significant fraction of thermal radiation from a sky-facing terrestrial object (at typical temperatures ~300 K) is not returned to it from the sky, effectively allowing such a surface radiative access to the universe. Beginning in the 1960s, researchers investigated exploiting this concept, known as radiative cooling, at night using black thermal emitters [1]. Moreover, it was noted early on that the spectral features of the atmosphere's transparency meant that a spectrally selective thermal emittance profile should allow a radiative cooler to reach lower temperatures [2]. Subsequent work thus tried to find materials with suitable emissivity profiles or to engineer selective emitters based on a thin film approach [3,4]. While over the last two decades, research interest in this topic declined, some recent work also examined the use of photonic nanoparticle effects for radiative cooling [5]. However, all of these efforts focused on radiative cooling at night, and until recently, radiative cooling during the day remained an open challenge.

Current and Future Challenges – If radiative cooling is to play a role in energy efficiency it is critical that it be accessible precisely at hours when the need for a colder cold sink is greatest: the day. Achieving radiative cooling during the day requires being able to maintain strong thermal emission, ideally selective to the atmospheric transparency window, while reflecting nearly all incident sunlight (Fig. 1). Our theoretical proposal [6] showed that daytime radiative cooling was indeed possible, and our recent experiment demonstrated [7] a performance of 5°C below ambient steady-state temperatures, and 40 W/m² cooling power at air temperature in clear sky conditions (Fig. 2). It is important to note however that this performance is strongly dependent on the infrared
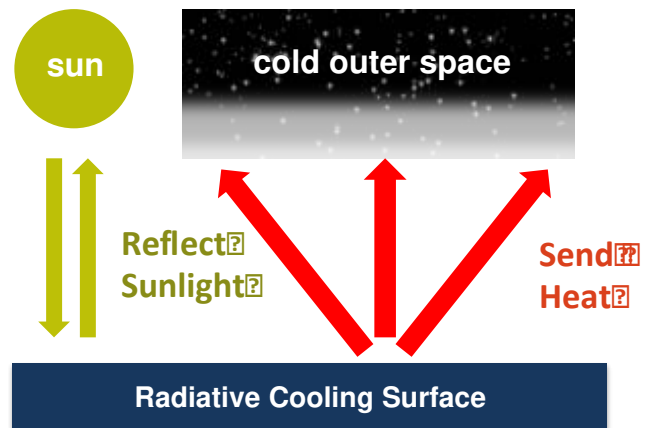

Figure 1 – Schematic of how a surface can cool itself radiatively below air temperature. Strong, selective thermal emission in the mid-infrared must be achieved while also reflecting nearly all incident sunlight.

properties of the atmosphere, which are in turn influenced by humidity and cloud cover. Under dry, hot conditions, better performance can be achieved with the same radiative cooler from Ref. [7]. In less favorable conditions, the net positive radiative flux at infrared wavelengths lessens, and an even higher solar reflectance is needed to achieve meaningful cooling power during the day. To further improve performance in all conditions, and enable useful cooling powers even in humid climates, achieving near-unity emissivity within the window is also important. While this is challenging, a recent paper demonstrated daytime cooling in challenging atmospheric conditions, offering cause for optimism [8].

Effectively using radiative cooling also entails minimizing parasitic heating from the environment. This is a non-trivial challenge given the constraints of operating under the sun, and the lack of cheap and rigid infrared-transparent materials that could serve as a window for the large areas typically needed. Making practical use of such surfaces for cooling also requires engineering systems that can efficiently transfer heat loads to the sky-facing surfaces while minimizing other heat gains. Radiative cooling systems will be particularly sensitive to such gains given that cooling powers available will typically be < 100 W/m².

In the demonstrations of daytime radiative cooling shown so far, the sunlight is reflected and goes unused. One challenge is thus to make use of this sunlight while preserving the cooling effect. In this spirit, we recently proposed the use of radiative cooling to cool solar cells [9] by engineering the thermal emissivity of a top surface above the photovoltaic material, while transmitting the same amount of sunlight through. This was one example of the broader vision of enabling and improving energy generation in addition to efficiency.

Related to this, there was also a recent proposal to make use of the imbalance between outgoing and incoming infrared thermal emission from sky-facing objects directly for energy conversion [10]. In both cases, experimental demonstrations pose challenges and are fruitful areas for further research.

Figure 2 – Outdoor test of a daytime radiative cooling surface. A test stand that insulates and minimizes parasitic heat gain is essential to maximize performance. A unique feature of radiative cooling experiments is the need to perform tests outdoors.

Advances in Science and Technology to Meet Challenges – A variety of photonic approaches can be leveraged to achieve both the spectral and angular selectivity desirable for radiative cooling [see sections 1, 13, 15-17]. A recent metamaterial-based design, for example, experimentally achieved extremely strong and selective emissivity within the atmospheric window [11].

Creative interdisciplinary research recently showed how the geometric shape and arrangement of hairs on Saharan silver ants not only increase their solar reflectance, but also their thermal emissivity in the mid-infrared, enabling their survival through cooling in very hot environments [12]. Such research opens up possibilities for biologically inspired metasurface designs that can achieve some of the same effects sought for radiative cooling during the day.

A key challenge, and opportunity, with radiative cooling will be to balance the need for low costs, for what is inherently a large-area technology, with the higher performance potentially achievable with more complex designs. While Ref. [7] showed that good

performance can be achieved with a non-periodic 1D photonic structure, recent advances in imprint lithography make more complex designs tractable given sufficient performance gains.

Concluding Remarks – Radiative cooling allows access to a thermodynamic resource of great significance that we have thus far not exploited in our energy systems: the dark universe. By effectively harnessing it during the day, we are not only able to access a universal heat sink precisely when it is most needed, but also demonstrate that such systems can have a 'capacity factor' of 24 hours a day – distinguishing this technology from photovoltaics. These demonstrations however are just the first building block in what we believe is a worthwhile and game-changing broader project: engineering all terrestrial energy systems to take advantage of this dark resource to improve their efficiency, and potentially directly generate energy as well. Improvements in spectral control of thermal emission through metamaterial and metasurface concepts could thus rapidly translate to improved performance both for direct cooling, and for indirectly improving the efficiency or generation ability of any terrestrial energy system.

References
[1] Trombe F (1967) Perspectives sur l'utilisation des rayonnements solaires et terrestres dans certaines régions du monde. *Revue Generale de Thermique* 6:1285.
[2] Catalanotti S, *et al.* (1975) The radiative cooling of selective surfaces. *Solar Energy* 17:83–89.
[3] Granqvist CG, Hjortsberg A (1980) Surfaces for radiative cooling: Silicon monoxide films on aluminum. *Appl Phys Lett* 36:139.
[4] Berdahl P, Martin M, Sakkal F (1983) Thermal performance of radiative cooling panels. *Int J Heat Mass Transf* 26:871–880.
[5] Gentle AR, Smith GB (2010) Radiative heat pumping from the Earth using surface phonon resonant nanoparticles. *Nano Lett* 10:373–379.
[6] Rephaeli E, Raman A, Fan S (2013) Ultrabroadband photonic structures to achieve high-performance daytime radiative cooling. *Nano Lett* 13:1457–61.
[7] Raman AP, Anoma MA, Zhu L, Rephaeli E, Fan S (2014) Passive radiative cooling below ambient air temperature under direct sunlight. *Nature* 515:540–544.
[8] Gentle AR, Smith GB (2015). A subambient open roof surface under the mid-summer sun. *Advanced Science* advs.201500119.
[9] Zhu L, Raman A, Wang KX, Anoma MA, Fan S (2014) Radiative cooling of solar cells. *Optica* 1:32–38.

[10] Byrnes SJ, Blanchard R, Capasso F (2014) Harvesting renewable energy from Earth's mid-infrared emissions. *PNAS* 111 (11) 3927-3932.

[11] Hossain MM, Jia B, Gu M (2015) A metamaterial emitter for highly efficient radiative cooling. *Adv Opt Mat* adom.201500119.

[12] Shi NN, Tsai C-C, Camino F, Bernard GB, Yu N (2015) Keeping cool: Enhanced optical reflection and heat dissipation in silver ants. *Science* aab3654.

20. Entropy Flux and Upper Limits of Energy Conversion of Photons – Gang Chen
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Status – The entropy of photons has been studied by many researchers in the past [1] [2], [3] [see section 1], but there are still unsettled questions. Understanding the entropy of photons will help set the correct upper limits in the energy conversion using photons, from solar cells to light-emitting diodes to optical refrigeration. We will use blackbody radiation as an example to lead the discussion. Considering an optical cavity of volume V at temperature T, the temperature and entropy (S) of photons inside the cavity obey the relation: TS=4U/3, where U(=4VσT⁴/c) is the internal energy of the blackbody radiation field inside the cavity, σ the Stefan-Bolzmann constant, and c the speed of light. While this relation is well-established, the trouble arises when one consider the thermal emission from a black surface with emissive power $J_b = \sigma T^4$ [W/m^2], with the corresponding entropy flux J_s

$$J_s = \frac{4}{3}\sigma T^3 = \frac{4}{3}\frac{J_b}{T} \qquad (1)$$

This expression does not follow the familiar definition for entropy flow across a boundary: Q/T, if the heat flow, Q, is set equal to the emissive power J_b. Wurfel [3] believes that one cannot define an entropy flux for thermal radiation. He argued that if the above relation is valid, one can devise a heat engine receiving heat flow by conduction and isentropically emitting out the entropy by thermal radiation, and generating useful work at same time, thus violating the 2nd law.

Current and Future Challenges – We argue that the entropy flux as defined in Eq. (1) is valid and the inequality between J_s and J_b/T is fundamentally due to the nonequilibrium nature of thermal radiation leaving a surface [4]. Consider that an object at temperature T receives heat Q at one boundary by conduction and emits as a blackbody thermal radiation via surface A, the rate of entropy generation in the process is, according to 2nd law of thermodynamics

$$\dot{S}_g = AJ_s - \frac{Q}{T} = \frac{1}{3}A\sigma T^4 \qquad (2)$$

If emission generates entropy, the reverse process should not work: an external blackbody radiation source is directed at an object, delivering radiant power $Q = A\sigma T^4$. This same of power cannot be conducted out, since otherwise, the process will leads to entropy reduction. The key to show this indeed the case is the Kirchoff law. We assume that the object's surface facing the incoming radiation is black. According to the Kirchoff's law, the object will also radiate back to the incoming radiation source (we will assume view factor of unity to simplify the discussion), so the net

heat that can be conducted out is: $Q = A\sigma(T_h^4 - T^4)$. Entropy generated in the object is then $\dot{S} = \frac{Q}{T} + \frac{4}{3}A\sigma T^4 - \frac{4}{3}A\sigma T_h^4$. This function is always positive, reaching a minimum when T=T$_h$ (and Q=0). Hence, the heat that can be conducted out is less than radiant power comes in (unless T=0 K).

At first sight, the idea that thermal emission from a surface generates entropy might be surprising. Careful examination, however, reveals that thermal emission from a surface is a sudden expansion of photon gas bearing similarity to the irreversible sudden expansion of gas molecules from a pressurized container to vacuum. Of course, there are also differences since photons normally do not interact with each other while molecules do. Hence, if a perfect photon reflector is placed in the path of the emitted photons to completely reflect back all photons leaving the black surface, there is no heat transfer and no entropy generation. In this case, photons at the emission surface are at equilibrium state and their temperature can be well-defined, and hence no entropy is generated. In the case of molecules expanding into a vacuum, it will be difficult to completely reflect back all molecules as they scatter each other and hence entropy will eventually be generated.

A standard way to make a black surface is a small opening on a large cavity. Immediately outside opening, photons only occupy isotropically only the half space since no other photons come in. The local temperature of photons cannot be defined, and correspondingly, one should not expect then J_b/T gives the entropy flux. If one is forced to use the local photon energy density to define a local equivalent photon temperature, this equivalent equilibrium temperature will be lower than T_h [5] [see section 1]. In this sense, it is not surprising that the entropy flux as given by Eq. (1) is larger than J_b/T_h.
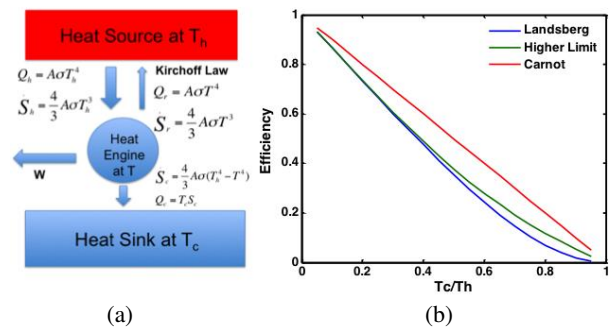

(a)   (b)

Figure 1 (a) A heat engine operating between a heat source at Th and a heat sink Tc. Heat transfer between the engine and heat source is coupled via thermal radiation. Kirchoff's law dictates that some photons and their associated energy and entropy are sent back to the heat source, (b) comparison of three different efficiencies, the Carnot, and Landsberg, and efficiency 2, which is higher than the Landsberg efficiency.

Although some researchers did use Eq. (1) for the entropy flux, they sometimes introduce a photon flux temperature T_f equaling to the ratio of J_b/J_s in the thermodynamic analysis of heat engines based on photons. Landsberg and Tonge [2] used the concept of photon flux temperature to derive the maximum efficiency of a heat engine at temperature T receiving thermal radiation from a heat source at temperature T_h as, $\eta_L = 1 - \frac{4}{3}\frac{T}{T_h} + \frac{1}{3}\left(\frac{T}{T_h}\right)^4$. This efficiency is called the Landsberg efficiency and has been derived by different researchers [4], [6]. As we will see later, although Lansberg and Tonge result is correct with proper interpretation (i.e., T equals the ambient temperature), their derivation did not in fact consider the ambient temperature (except in an alternative availability argument). We will re-derive below the Landsberg limit and also show a higher limit when the radiation source is not from the sun.

Our model considers a thermal emitter coupled to a heat reservoir at temperature T_h, and heat engine at temperature T (our results are valid if T is time varying but we will not include time here for simplicity), and a cold reservoir at T_c as shown in Fig. 1(a). We assume the surfaces involved in the radiative heat transfer between the heat reservoirs are blackbodies. The key is to recognize that when a heat engine absorbs thermal radiation, it also radiates back to the thermal emitter according to the Kirchoff's law as illustrated in Fig.1(a). Correspondingly, the net rate of entropy flowing into the heat engine is $\dot{S}_{in} = \frac{4}{3}A\sigma\left(T_h^3 - T^3\right)$. The maximum power is reached when this entropy is rejected to the cold reservoir T_c without additional entropy generation in the heat engine and the heat rejection process. The rate of heat rejection is then, $Q_c = T_c\dot{S}_{in} = \frac{4}{3}AT_c\sigma\left(T_h^3 - T^3\right)$. The power output can be obtained from the first law analysis for the heat engine:

$$W = Q_h - Q_r - Q_c = A\sigma T_h^4\left(1 - \frac{4}{3}\frac{T_c}{T_h}\right) - A\sigma\left(T^4\frac{4}{3}T_cT^3\right)$$

The above expression is maximum when $T=T_c$,

$$W_{max} = A\sigma T_h^4\left(1 - \frac{4}{3}\frac{T_c}{T_h}\right) + \frac{1}{3}A\sigma T_c^4 \qquad (3)$$

We can define two efficiencies using the above analysis. One is based on the radiant energy leaving the heat reservoir,

$$\eta_1 = \frac{W_{max}}{A\sigma\Delta t T_h^4} = 1 - \frac{4}{3}\frac{T_c}{T_h} + \frac{1}{3}\left(\frac{T_c}{T_h}\right)^4 \qquad (4)$$

This expression is but the Lansberg efficiency. This efficiency definition is appropriate for solar radiation. However, if the thermal emission comes from a terrestrial heat source such as in a thermophovotovoltaic device [see sections 15-18], the heat supplied to the heat reservoir should be the difference of radiated and absorbed radiation by the reservoir, $Q = A\sigma\left(T_h^4 - T_c^4\right)$ and the efficiency should be defined as

$$\eta_2 = \frac{W_{max}}{Q} = \left[1 - \frac{4}{3}\frac{T_c}{T_h} + \frac{1}{3}\left(\frac{T_c}{T_h}\right)^4\right]\left[1 - \left(\frac{T_c}{T_h}\right)^4\right]^{-1} \quad (5)$$

This efficiency is higher than the Landsberg efficiency. Thus, although the Landsberg efficiency is appropriate for solar radiation and is often considered as an upper limit for thermal radiation-based energy conversion systems, a higher limit exists when terrestrial heat sources are used as the photon source.

Advances in Science and Technology to Meet Challenges – Our discussion so far has limited to the blackbody radiation. We believe that the same strategy can be applied to search for the upper limits of all other photon-mediated energy conversion processes involving nonblack objects, emission from solar cells, light emitting diodes, lasers, photosynthesis, optical upconversion, optical refrigeration, [7], [8] near-field radiation heat transfer, and near-field to far-field extraction, etc.. For analyzing these processes, one should bear in mind two key results obtained from past studies. First, a general expression for the entropy of photons in a quantum state, whether they are at equilibrium or not, is $S_1 = k_B[(1 + f)\ln(1 + f) - f\ln f]$, where f is the number density of photons in the quantum state. From this expression, one can obtain entropy flux leaving a surface by considering the velocity of photons, and summing up all their quantum states [2]. The other key result is photons possess an effective chemical potential when the radiation field is created via recombination of excited states at different chemical potentials [see sections 1,4,18], although purely thermally radiated photons do not have a chemical potential ($\mu=0$) since their numbers are not fixed. This fact is used in analyzing photon based energy conversion processes and devices such as phovoltaic cells, [9] light emitting diodes, photosynthesis, etc.. However, there does not seem to be studies starting from the entropy flux consideration to arrive at the maximum efficiency of energy conversion processes. The Shockley-Queisser limit [10] for photovoltaic cell, for example, is based on consideration of the balance of photon and charge number densities.

Concluding Remarks – In summary, thermal emission from a surface is a nonequilibrium process involving entropy generation. For blackbody radiation, the entropy flux expression, i.e., Eq. (1), is valid. By considering the entropy flux of photons, one can arrive at proper upper limits for different photon-based energy conversion devices. More research along this

direction can stimulate further advances in photon-based energy conversion.

References
[1] L. Landau and E. Lifshitz, *Statistical Physics, Part 1*. 1980.
[2] P. T. Landsberg and G. Tonge, "Thermodynamic energy conversion efficiencies," *J. Appl. Phys.*, vol. 51, no. 7, 1980.
[3] P. Wurfel, "The chemical potential of radiation," *J. Phys. C Solid State Phys.*, vol. 15, no. 18, pp. 3967–3985, 2000.
[4] R. Petela, "Exergy of Heat Radiation," *J. Heat Transfer*, vol. 86, no. 2, p. 187, 1964.
[5] G. Chen, *Nanoscale Energy Transport and Conversion*. Oxford University Press, 2005.
[6] H. Mashaal and J. M. Gordon, "Basic limit for the efficiency of coherence-limited solar power conversion," vol. 39, no. 17, pp. 5130–5133, 2014.
[7] M. Sheik-Bahae and R. I. Epstein, "Optical refrigeration," *Nat. Photonics*, vol. 1, no. 12, pp. 693–699, 2007.
[8] C. E. Mungan, "Thermodynamics of radiation-balanced lasing." J. Opt. Soc. Am. B/Vol. 20, No. 5/May 2003.
[9] C. H. Henry, "Limiting efficiencies of ideal single and multiple energy gap terrestrial solar cells," *J. Appl. Phys.*, vol. 51, no. 8, pp. 4494–4500, 1980.
[10] W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," *J. Appl. Phys.*, vol. 32, no. 3, pp. 510–519, 1961.