

HARVESTING SUNSHINE: SOLAR CELLS, PHOTOSYNTHESIS AND THE THERMODYNAMICS OF LIGHT

T. Markvart, L. Danos, N. Alderman, L. Fang and T. Parel
Solar Energy Laboratory, School of Engineering Sciences, University of Southampton,
Southampton SO17 1BJ, UK.

ABSTRACT: Effective capture of sunlight represents one of the grand challenges of photovoltaics today. This paper looks at the opportunities that exist, at the fundamental level, to manage light as the first step of photovoltaic conversion; in particular, how photonics can improve the efficiency and reduce the cost of solar cells. Starting from the current view of light trapping we shall introduce an additional variable: photon frequency. The example of fluorescent collectors will be used to discuss the principal features of frequency management, leading to a novel form of light trapping and, ultimately, the photonic bandgap solar cell. The discussion will be guided by arguments based on thermodynamics to describe photon transformation as part of the absorption / emission / conversion process. By drawing parallels with the capture of light in photosynthetic organisms we shall briefly discuss another important aspect: light harvesting energy collection, and the opportunity this represents for reducing the materials usage in future generations of solar cells.

Keywords: Fundamentals, light trapping, optical losses, high efficiency, light harvesting, photonics.

1 INTRODUCTION

Effective capture of sunlight represents one of the grand challenges of photovoltaics today. Although ancestors of these techniques have been known for hundreds if not thousands of years, modern photovoltaics is now offered a rich landscape of tools and methodologies of how this field can be amplified and expanded. Many solar cells today, for example, rely on light trapping to enhance optical absorption. Fluorescent collectors represent an opportunity to capture and concentrate light by manipulating its frequency. Perhaps not so well known to the photovoltaic research community is light harvesting which is used to advantage in photochemistry.

We shall see that, by and large, light capture can be discussed independently from the next essential step in the conversion process – charge separation. Moving forward into the future one can imagine a new generation of solar cells where photovoltaic conversion takes place in two distinct parts of the device, with an absorber / energy collector efficiently absorbing light and transferring energy to a conversion part of the device which separates the photogenerated charges and produces electricity. Each part of the structure can be optimised independently, leading to efficient light absorption and energy conversion within a compact device, with low material requirements and low cost.

This paper will review a range of modern light management techniques with the aim of finding a common ground among many of the structures and techniques that are being studied today in research laboratories. We shall discuss useful clues that emerge from parallels with classical thermodynamics and heat engines, photonics and photonic crystals, and with a natural - and very ancient - solar energy conversion system: photosynthesis.

2 LIGHT TRAPPING

Light trapping is a common feature of many solar cells made from crystalline silicon as well as other materials where the reduction of thickness represents a key target for reducing the cost or improving the performance in other ways. A convenient view for the

analysis of light trapping is to consider the solar cell as a waveguide. A general argument divides the modes of electromagnetic field inside such structure into modes that spread out into the external space occupied by the radiation field (the radiation or external modes), and those that are trapped inside the waveguide (internal or trapped modes). If we suppose that only the top face of the cell/waveguide (of area A , say) is exposed to external radiation and other faces are covered by mirrors, the classical diagram divides the two bundles of rays by the angle θ_c for total internal reflection (Fig. 1a). Clearly, the very long (at the first sight, infinite) optical path length of photons in the trapped modes provides an opportunity to improve light absorption in weakly absorbing media. However, photons have to be transferred into these modes and this can only be done by processes outside the realm of geometrical optics - for example, by scattering. In practice, light is usually scattered by a top surface texture although rear surface texturing or scattering by other objects produces similar results (Fig.1 b).

Mechanisms that populate the trapped modes (such as scattering) introduce a statistical element into the analysis. These processes are governed by microscopic reversibility (or detailed balance) which implies that scattering occurs into as well as out of these modes, with equal probability. This first indication of thermodynamics gives us an important clue that photons will eventually reach an equilibrium - in this instance, a isotropic distribution with respect to all directions. It is then easily shown that the maximum photon path length inside a layer of thickness d is equal to [1, 2]

$$\ell_{\max} = 4dn^2 \rightarrow 4d \frac{\pi n^2 A}{\mathcal{E}_{\text{out}}} \quad (1)$$

where n is the refractive index of the medium and d is the thickness of the structure. The second equation (1) shows how the path length can be increased further by restricting the angular range of the emitted beam to a narrower cone that given by the critical angle θ_c for total internal reflection – in other words, by restricting the *size* of the emitted beam, or its *étendue* \mathcal{E}_{out} .

The étendue is a useful concept for a number of reasons. It is conserved in a clear, non-absorbing and non-scattering medium and an invariant in geometrical optics

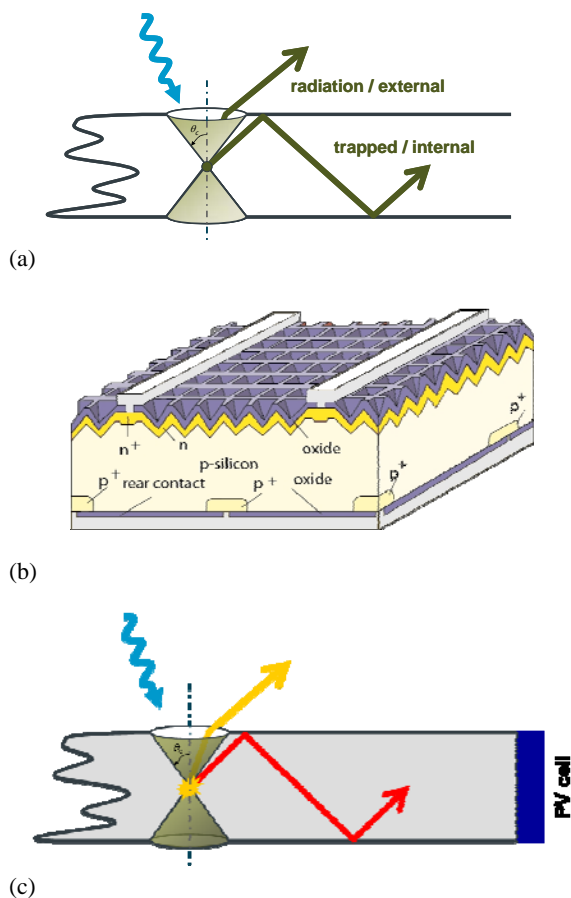


Figure 1: (a) Radiation and trapped modes in a thin dielectric layer. (b) UNSW PERL cell [3] with a textured top surface to improve light absorption by scattering into the trapped modes. (c) Light trapped by absorption and re-emission at a longer wavelength, illuminating a solar cell at the edge of a fluorescent collector.

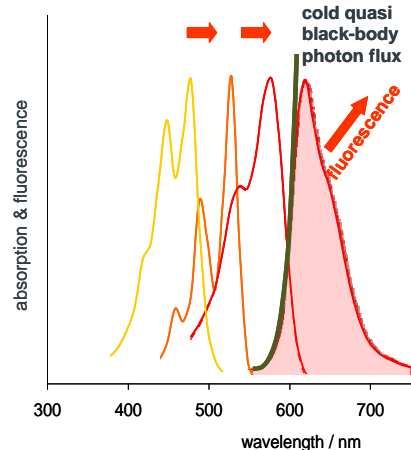
[4]. From a different viewpoint, the étendue is a measure of the volume that the beam occupies in the phase space of geometrical and angular coordinates, and thus – in the semi-classical picture – also a measure of the number of photon states in the beam. This latter characteristic provides the foundation for a statistical description and a definition of the entropy [5]. The étendue of a beam incident from a full hemisphere is equal to $\pi r^2 A$. Equation (1) can then be understood by noting that the last term is just the ratio of the number of states for photons incident onto the top surface inside the layer to the number of radiation modes. We shall see how the étendue and entropy can be applied to the efficiency of solar cells in Sec. 4.

3 FLUORESCENT ENERGY COLLECTORS

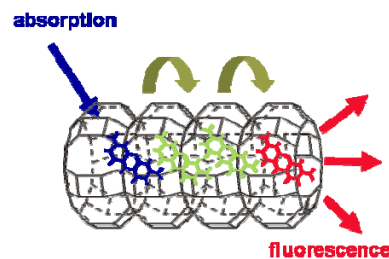
The picture of light trapping discussed in the previous section can be generalised by including another important variable that pertains to the beam: its frequency. A structure based on this philosophy is usually called fluorescent concentrator or collector (Fig.1c). Fluorescent collectors absorb light through the front face, with the aim to capture the re-emitted fluorescent light at the edge

of the structure by a solar cell [6, 7], although other geometries also possible [8].

Trapping light into the guided modes in fluorescent collectors takes place by light absorption and subsequent re-emission, in contrast with the scheme of Fig.1,a,b where the trapped modes are populated by scattering. Notwithstanding, the fundamental loss mechanism is similar in both cases – photon emission within the escape cone corresponding to the front surface (the entrance aperture). This is so at least in good collectors which contain dyes with a quantum yield close to unity



(a)



(b)

Figure 2: (a) The absorption spectra of molecules acting as stepping stones in a sequence of energy transfer steps. The energy is eventually emitted as fluorescence which, when re-absorbed, emerges as thermal radiation with a finite chemical potential [11]. (b) The same process as in (a) but pictured as excitation energy transport in space between molecules embedded in zeolite L [10].

There are also important differences between the two schemes. Frequency and photon energy are conserved in geometric light trapping schemes. In contrast, each absorption/emission event changes photon energy, and the relationship between the absorption and emission spectra in the fluorescent collector has to be carefully controlled to achieve efficient operation [6,7]. The capture of the broad incident solar radiation spectrum usually requires a mixture of dyes which can channel energy to a single level for fluorescence (Fig. 2a). An effective vehicle for this purpose is the so-called resonance or Förster energy transfer [9]. Efficient photon management without radiationless losses can then be achieved by embedding a suitable mixture of dyes in a structured medium which allows the creation of a specific environment of the molecules as well as maintaining optimum separations between them.

We note here an interesting parallel: Förster energy transfer not only changes the emission spectrum (Fig. 2a) but can be used to transport energy in space (Fig.2b). This effect has been demonstrated in a particularly elegant way by Gion Calzaferri and his group at Berne University by forming structured complexes of molecules with the help of zeolites [10]. We shall return to this energy transfer aspect when we discuss light harvesting in Sec. 5.

From a thermodynamic perspective, each absorption / emission event can be viewed as a transition between two photon states which complies with the thermodynamic condition of detailed balance [12]. This condition guarantees approach to equilibrium – in this instance, a full thermodynamic equilibrium rather than simply an isotropic distribution at a single frequency, and confirmed also experimentally by observing the photon flux emitted from the edge (Fig. 2a) [11]. Where reabsorbed, the spectrum re-emitted photons has been shown to follow a thermal distribution similar to the black body radiation but with a temperature close to the temperature of the absorbing / emitting material.¹ Unlike the incident solar beam, this radiation has a non-zero chemical potential.

The frequency management process has been illustrated here on the example of energy transfer between localised molecular states but this is exactly what happens in a solar cell immediately after light absorption, during what is usually called the “thermalisation” of electron hole pairs. The difference is that here the process is much slower (on a time scale of nanoseconds rather than picoseconds) and can be controlled to a much higher degree by changing the molecular species and their separation. This offers an opportunity for the absorber of solar radiation to retain some of the heat that it receives during the capture process. It is worthwhile to explore this avenue in more detail and divert our discussion to consider, albeit briefly, the operation of a solar cell in thermodynamic terms.

4 SOLAR CELL AS A HEAT ENGINE

Thermal equilibrium among photons brought about by reabsorption (also known as photon recycling) is a familiar process which occurs in a solar cell prior to charge separation, providing the foundation for the Shockley - Queisser detailed balance model of solar cell efficiency [13]. We can conjecture that the results obtained by Shockley and Queisser using a kinetic theory could also be obtained by an argument based on thermodynamics, and this is indeed the case. The picture of solar cell that emerges is very similar to a heat engine, converting solar radiation (modelled as a black body radiation at temperature T_s near 6000K) into thermal radiation at ambient temperature ($T_o \sim 300$ K) and work (Fig. 3). The work that can be carried out per photon - determined here by the voltage produced by the solar cell - is equal to the chemical potential of the emitted photons which we have already encountered in the operation of fluorescent collectors.

What is remarkable is that this picture is independent of the structure of the solar cell: the only parameter that enters the calculation is the bandgap of the semiconductor to define the energy band of the incident and

emitted photon fluxes. Thermodynamics can then be used to identify separately the fundamental losses in terms of irreversible entropy generation simply by considering the cooling of photon from temperature T_s to T_o [14,15]. As some of these losses are avoidable, the thermodynamic methodology can help us progress beyond the Shockley-Queisser limit to higher efficiency devices, for example, hot carrier solar cells.

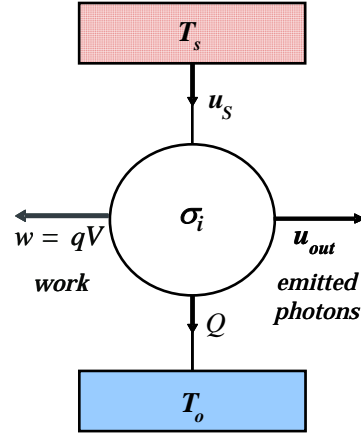


Figure 3: The heat engine model of a solar cell [15].

In thermodynamic terms (Fig.3), solar cell operation involves the absorption of solar heat (energy u_s per photon) which is converted into work (equal to the electrostatic energy qV , where V is the voltage and q is the electron charge), emitting photons alongside the conversion process. For each photon converted to electricity, heat Q is rejected to a reservoir at ambient temperature T_o , generating entropy σ_i due to irreversible losses. The resulting thermodynamic equation for solar cell voltage can be written in the form

$$qV = u_s \left(1 - \frac{T_o}{T_s} \right) - T_o \sigma_i \quad (2)$$

which bears a remarkable similarity to the equation used to explain the operation of a heat engine in mechanical engineering. Contributions to entropy generation σ_i include:

- Nonradiative losses which can, in principle, be reduced or eliminated by improving material quality;
- The solar cell has to produce finite current, and the “conversion engine” therefore has to operate at a finite speed. In thermodynamic terms, this generates entropy which describes the I-V characteristic and the fill factor.
- The conversion process expands the beam of light, increasing the étendue from ξ_{in} for the incident beam, to ξ_{out} on emission, and generating entropy σ_{exp} [15]:

$$\sigma_{exp} = k_B \ln \left(\frac{\xi_{out}}{\xi_{in}} \right) \quad (3)$$

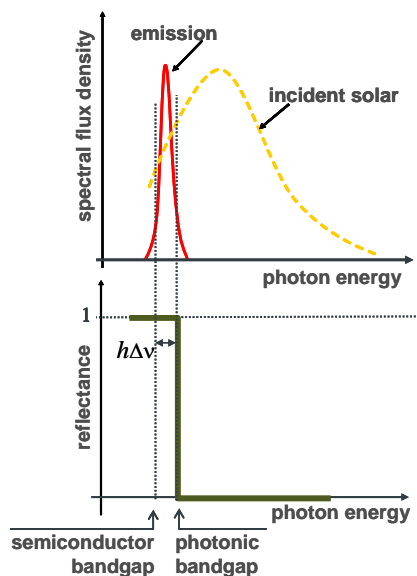
This entropy can be reduced or eliminated by concentrating sunlight, i.e. by increasing the étendue of the incident light or restricting the étendue of the emitted beam;

¹ More correctly, the Kennard-Stepanov temperature [12]

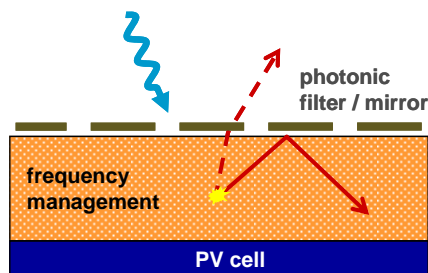
- Photon cooling or thermalisation (already alluded to in Sec. 3) generates entropy σ_c which can be determined using ideal gas theory [15]:

$$\sigma_c = k_B \left(\frac{T_s}{T_o} - 1 \right) - k_B \ln \left(\frac{T_s}{T_o} \right) \quad (4)$$

We can therefore speculate that, in a future *hot carrier solar cell*, voltage can be increased by an amount equal to $T_o \sigma_c / q$, where σ_c is given by (4). This would be an almost 50% improvement for a crystalline silicon solar cell under one-sun illumination, providing a target if not a guide for research into the next generation of photovoltaic devices.



(a)



(b)

Figure 4: (a) Top: Absorption and fluorescence spectra of a photon management structure discussed in Sec. 3; Bottom: The reflectance spectrum of a photonic structure for efficient trapping of the fluorescent light. (b) A schematic diagram of the photonic bandgap solar cell.

5. THE PHOTONIC BANDGAP SOLAR CELL

Returning to the light-trapping theme and its link to photon management we may intuitively expect that the thermalisation of photon gas provides an opportunity to improve the efficiency of light trapping in these structures and thus reduce the material requirements (and

hence reducing the cost) of solar cells. We shall now show how this opportunity can be exploited - with the help of photonics.

Recent advances [16] make it possible to manufacture three dimensional photonic crystals that reflect light selectively in a specific spectral range, independently of the angle of incidence (Fig 4). Suppose now that the spectral range of such a photonic band stop is tuned to coincide with the emission wavelength of the frequency management structure. If placed to cover the illuminated surface, the photonic crystal will transmit most of the broad solar spectrum but reflect the narrow-band fluorescent light, effectively trapping this light inside the structure. The confinement is not absolute, of course but to escape, photons need to extract heat from the absorbing medium, making light emission from the structure a much slower process.

We can compare this photonic light trapping scheme with the usual surface texture scattering scheme. It can be shown that the frequency shift in the photonic scheme extends the photon path length further by a factor equal to an inverse of the Boltzmann factor appropriate to the frequency band width of the trapped light [17]:

$$\ell_{\max} \cong 4n^2 d e^{h\Delta\nu/k_B T_o} \quad (5)$$

If the width of the frequency band stop $\Delta\nu$ is large, the photonic structure would block a large part of the spectrum but, as we shall see presently, there is an optimum value which transmits a sufficient part of the solar spectrum whilst ensuring a substantial enhancement in light trapping.

This is illustrated in Fig. 5 which shows the quantum efficiency of a crystalline silicon solar cell based on the scheme of Fig. 4b compared with more conventional arrangements. The photonic band stop blocks light between 900 nm and 1100 nm, corresponding to the silicon bandgap of 1.12 eV. We observe that the photonic bandgap now takes over from the electronic bandgap of silicon as the principal parameter which describes the quantum efficiency. Furthermore, the frequency band stop ensures a near perfect light trapping, and although light between 900 nm and 1100 nm is reflected from the structure, light with wavelength below 900 nm is absorbed and utilised with quantum efficiency close to unity. This is the case even though the cell thickness is merely $1\mu\text{m}$ and the absorption length in silicon at the wavelength of 900 nm is almost $30\mu\text{m}$.

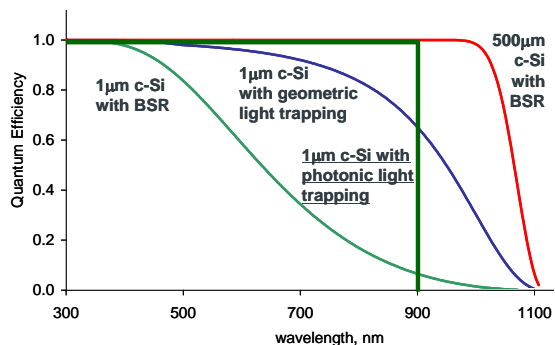


Figure 5: The quantum efficiency of the photonic bandgap solar cell in Fig. 4b, compared with an ideal $500\mu\text{m}$ crystalline silicon solar cell, a $1\mu\text{m}$ c-Si solar cell with a back-surface reflector and with a geometric (surface texture) light trapping scheme [18].

Table I: Efficiencies of solar cells in Fig. 5.

500 μm c-Si cell	30.3%
1 μm cell (BSR only)	15.6%
1 μm cell (geometric light trapping)	26.0%
1 μm cell (photonic light trapping)	30.7%

The efficiencies of solar cells shown in Fig. 5 obtained with the use of modelling are shown in Table 1. What is most surprising is that the efficiency of a 1 μm solar cell with photonic light trapping is higher even than the efficiency of an ideal conventional thick crystalline silicon solar cell. Without pursuing this matter any further (suffice it say that the answer lies in the shape of the Shockley-Queisser efficiency graph as a function of bandgap energy !) we turn to another mechanism how light capture in solar cells may be enhanced: by learning from photosynthesis.

6 PHOTOSYNTHESIS AND LIGHT HARVESTING

Photosynthesis is well known as a process that creates oxygen and carbohydrates from water and carbon dioxide. What is less frequently mentioned is that the primary energy conversion step in photosynthesis involves a set of oxidation - reduction reactions, i.e. electron transfer. An electron is removed from water and, after acquiring the energy of two light quanta, reduces a nicotinamide compound which then provides energy to transform carbon dioxide into carbohydrates. Each of the two photochemical reactions transfers an electron across the photosynthetic membrane, in a process that bears many similarities with a solar cell. In fact, by tampering with the system, the membrane can produce electrical energy, in the form of an electrostatic potential [19].

The main point that we will focus on here is that the photochemical reaction is not driven by a direct absorption of a photon. Instead, photons are absorbed by one of several hundred chlorophyll (or other auxiliary pigment molecules) and transferred to the reaction centre by *light harvesting*. In fact, we have already encountered a similar process in the discussion of photon management – energy collection via non-radiative Förster energy transfer. Förster transfer is induced by the near-field interaction between the transition dipole moments on the participating molecules, and bears many similarities with phenomena discussed in the optics of nanostructures where much of the detail is still the subject of extensive research. What has been clearly demonstrated, however, is that light harvesting via energy transfer delivers efficiently the energy required for a photochemical reaction and enhances the optical capture cross section of photosynthetic charge separation by several orders of magnitude.

We have already seen that the light-harvesting structures can be made in the laboratory but why stop there ? The photochemical reaction separates charges across the photosynthetic membrane. There is no reason why a similar light harvesting process cannot be used to supply energy and excite an artificial charge separation unit made from semiconductor – for example, a p-n junction. The resulting solar cell would benefit from

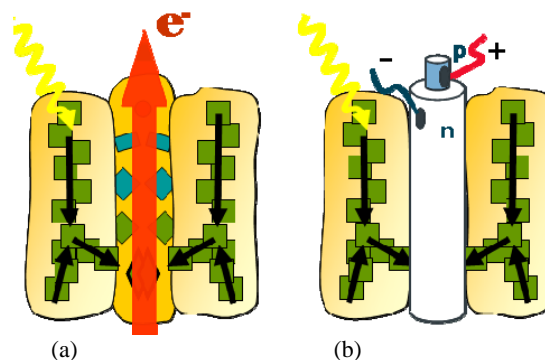


Figure 6: (a) A schematic diagram of light harvesting supplying energy to the primary photochemical redox reaction in photosynthesis. (b) A future solid-state photovoltaic generator ?

excellent optical properties of the molecular light harvesting unit (which, in the future, could be made from quantum dots) and the efficient charge separation attributes of a semiconductor device [20,21]. This is particularly relevant for indirect gap semiconductors such as silicon as this mechanism potentially by-passes the selection rule which hinders absorption of light in these materials.

7 CONCLUSION

This paper has discussed a number of strategies for improving the capture of solar radiation. Similarities between light trapping and fluorescent energy collection help us understand how to enhance the photon path length inside a solar cell and improve photoexcitation of poorly absorbing materials such as crystalline silicon. We have shown how optimum operation of such structures can be achieved with the help of photonic crystals. The resulting photonic bandgap solar cells can not only achieve efficiencies comparable with their conventional counterparts but potentially lead to a substantial reduction in the usage of silicon and hence to a considerable reduction in cost.

We have seen how a detailed understanding of fundamental losses in photovoltaic conversion can be achieved with the help of thermodynamics, paving the way for increasing efficiency above the Shockley-Queisser limit in, for example, hot carrier cells.

Efficient capture of solar radiation occurs as the first processes of the photochemical reaction in photosynthesis, in a process known as light harvesting. The combination of light harvesting with charge separation at a semiconductor junction can not only dramatically improve solar energy capture but provides clues about the energy aspects of light interactions with matter on the nanoscale.

At the fundamental level, much can be gained by separating the photovoltaic conversion process into light capture and charge separation, each part making use of different structures and different materials, bringing a new dimension to be explored in future generations of cheap and efficient solar cells.

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