Photon management: from Kirchhoff and Planck to solar cells

Tom Markvart

Engineering Sciences, University of Southampton, Southampton SO17 1BJ, UK and Centre for Advanced Photovoltaics, Czech Technical University, 166 36 Prague 6, Czech Republic

The manipulation of light provides an attractive option to enhance the output of a solar cell. Optical concentration, antireflection coatings, light trapping and fluorescent collectors are just few examples of technologies in routine use or under discussion in many research laboratories today. Although these techniques are relatively recent, the physical principles date back to a much earlier date, and have much in common with the thermodynamic foundations of the quantum theory.

An important facet of photon management is expressed by the relationship between the absorption and emission of light (Fig. 1). Kirchhoff's law¹ (but see also ref²) - which brings attention to the emission from a surface - was subsequently revised by Planck,³ ascribing absorption and emission to a volume. Einstein⁴ expressed Planck's balance between the volume absorption and emission rates to quantum states discovering, at the same time, stimulated emission which later paved the way to the invention of laser. Einstein's relation was applied to radiative transitions at molecules by Kennard⁵ and Stepanov,⁶ and to semiconductors by van Roesbrook and Shockley.⁷



Fig. 1. Different views of the reversibility between absorption and emission of radiation (adapted from Ref. 8). Photon management in solar cells usually concerns the balance between surface and volume absorption/emission characteristics (blue arrows).

Many applications of photon management concern photon transport in the material between the surface and volume absorption or emission (Fig. 1). The different optical parameters are mutually interdependent, as becomes apparent from a recently derived balance relation between surface and volume absorption:⁹

$$1 - r = \frac{a}{\ell_{opt}\alpha} \tag{1}$$

where *r* is the probability of reabsorption of the emitted photons, α and *a* are the absorption coefficient and absorptivity at the emission wavelength, and we introduced a quantity $\ell_{opt} = 4\pi n^2 V/\mathcal{E}$ with the dimension of length, where *V* is the volume of the structure, \mathcal{E} is the étendue of the emitted beam and *n* is the refractive index. For a planar structure of thickness *d*, ℓ_{opt} reduces to $4n^2d$. If we identify photons in textured solar cells as Planck's "photon gas", Eq. (1) immediately yields the enhancement of absorption as given by Tiedje et al¹⁰ (see also ref. 8). For high absorption (*a* ~ 1), Eq. (1) yields a "universal" law¹¹ for reabsorption in the black body limit. Most of the talk will focus on various aspects of photon reabsorption, often now referred to as photon recycling. Starting with the principal attribute of photon recycling - the manifestation of the interaction between light and matter that brings photons into thermal equilibrium (Fig. 2) - we shall discuss several questions which have recently been raised, including: does photon recycling concentrate light ? Does it enhance the open circuit voltage ?



Fig. 2. Rhodamine 6 G absorption and fluorescence (points, experiment, and thick red line, theory). Fluorescence from the edge of a flat planar slab under high reabsorption approaches the (quasi) black body radiation at room temperature.¹²

<u>Acknowledgement:</u> Centre for Advanced Photovoltaics is supported by the Czech Ministry of Education, Youth and Sport. CZ.02.1.01/0.0/0.0/15_003/0000464.

References

- ¹ G. Kirchhoff, On the relation between the radiating and absorbing powers of different bodies for light and heat (translation of a German original), Phil. Mag, Ser. 4, 1860, 20: 1.
- ² Balfour Stewart, An account of some experiments on radiant heat, involving an extension of Prévost's theory of exchanges, Trans. Roy. Soc. Edinburgh, 1857-61, 22:1.
- ³ M Planck, The Theory of Heat Radiation (English translation) Dover, New York, 1991.
- ⁴ A. Einstein, On the quantum theory of radiation, Phys. Z. 1917, 18:121. English translation in B.L. van der Waerden, Sources of Quantum Mechanics, Dover, New York, p. 63.
- ⁵ E.H. Kennard, On the thermodynamics of fluorescence, Phys. Rev. 1918, 11:29; On the interaction of radiation with matter and on fluorescent exciting power, Phys. Rev. 1926, 28: 672.
- ⁶ B.I. Stepanov, A universal relation between the absorption and luminescence spectra of complex molecules, Sov. Phys.- Dokl. 1957, 112:81; Correlation between the luminescence and absorption spectra of complex molecules, Izv. Akad. Nauk SSSR 1958, 22:1357.
- ⁷ W. van Roosbroeck and W. Shockley, Photon-radiative recombination of electrons and holes in germanium, Phys. Rev. 1954, 94:1558.
- ⁸ T. Markvart, From steam engine to solar cells : can thermodynamics guide the future generations of photovoltaics ? WIREs Energy Environ 5, 543 (2016)
- ⁹ T. Markvart, Radiative balance between photon emission from surface and in volume, arXiv:1612.01384 (2016)
- ¹⁰ T. Tiedje, E. Yablonovitch, G.D. Cody and B.G. Brooks, Limiting efficiency of silicon solar cells, IEEE Trans. Elec. Dev. **31**, 711 (1984)
- ¹¹ L. Fang, T. S. Parel, L. Danos and T. Markvart, Photon reabsorption in fluorescent solar collectors, J. Appl. Phys. 111, 076104 (2012).
- ¹² T.J.J. Meyer and T. Markvart, The chemical potential of light in fluorescent solar collectors, J. Appl. Phys. **105**, 063110 (2009).