THE QUEST FOR VERY HIGH EFFICIENCY IN PHOTOVOLTAIC ENERGY CONVERSION

* **Jean-François Guillemoles**
* Institut de Recherche et Développement sur l'Énergie Photovoltaïque • IRDEP, UMR 7174 CNRS-EDF-ENSCP, 11 Quai Watier, 78401 Chatou cedex • E-mail: jf-guillemoles@chimie-paristech.fr

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Photovoltaic conversion of solar energy could be much more effective than it is currently, using basic P-N junctions. The approaches to reach the conversion limits (~90%) are very challenging. Some have already been demonstrated (multi-junctions). Others, with the description of excited states in condensed matter and nanosciences having improved considerably, are only waiting for bold scientists…

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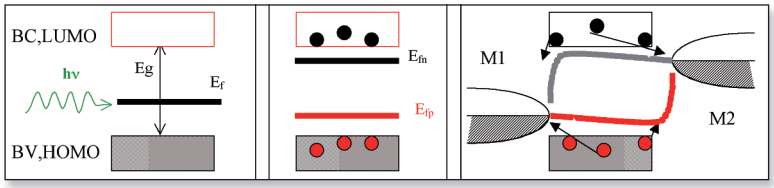
Like any conversion system of energy, a photovoltaic generator has its performances limited by the laws of thermodynamics. In a first approach, one can regard the sun as a hot source with T = 6000 K, the cold source being the environment (T_e ~ 300 K). The Carnot efficiency of the solar energy conversion is 95 % in theory! However, today's best photovoltaic devices, semiconductor photodiodes, achieve efficiencies of only 20-25 %. The difficulty lies with the optimal conversion of a whole range of photons whose energy goes from the infrared to the ultraviolet, with only one active material whose optical properties can be optimally adapted only to a given photon energy (the absorption threshold, or energy gap, E_g). To understand why, we must return to the principles of photovoltaic conversion [1], such as the devices currently used.

This conversion is done in three stages (fig. 1): (a) absorption of photons of energy $h\nu > E_g$, which creates populations of electrons and holes out of equilibrium; (b) each type of carriers very quickly reaches steady state defined by a quasi-Fermi level E_{fn} for the electrons and E_{fp} for the holes, whose difference, $E_{fn} - E_{fp} = qV$, is the recoverable free energy from photon absorption (V is the photovoltage); (c) the carriers, collected by the contacts before they can recombine, participate in the photocurrent.

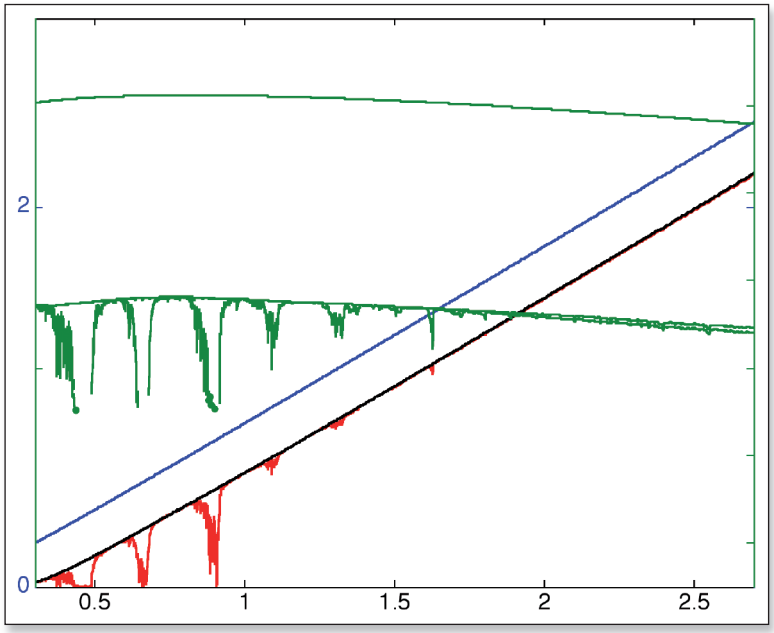
Photovoltaic devices are rather similar to an electrochemical battery: only their anode and their cathode consist of different energy levels from the same material. In this device, one must have $h\nu > E_g$ because of the properties of absorption, but also $E_g > E_{fn}$-E_{fp}[1]. The fraction of energy which can effectively be converted by an absorbed photon, qV/hν, is therefore much smaller than its maximum value, because the free energy obtained from each photon is independent of its energy (the remainder goes to the atomic lattice heat in less than a few picoseconds, during the carriers thermalisation). Including that part of the photons that is not absorbed, the efficiency is limited to 30 % for the optimal gap E_g and under standard conditions of illumination [1]. Since the quasi-Fermi levels depend on the charge carriers concentration[2], which in turn depends on the light flux, it follows that the recoverable free energy per incident photon increases with their flux: it is advantageous to concentrate the solar flux before conversion. The potential efficiency gain is 3 percentage points per decade.

Note that the maximum concentration of solar flow is limited to a factor of 42 600[3] by thermodynamics: the image of an object cannot be hotter than the object itself[4]. One can calculate the maximum value of free energy which can be extracted for each absorbed photon (fig. 2), independently of the conversion system [2]. This free energy depends solely on the energy of the photon and the incident flux. With the help of figure 2, one calculates that the maximum efficiency of a photovoltaic device is 67 % under standard solar illumination and 87 % under maximum concentration. If no such efficiencies could have been approached yet, it is because the materials and technologies were not ready to meet the severe specifications necessary.



▲ **FIG. 1: Principle of photovoltaic conversion, broken up into three principal stages. (a) Absorption of a photon and promotion of an electron to a higher and empty level. (b) Establishment of two populations of electrons and holes in internal quasi-equilibrium (via fast, ps, relaxation processes), but unbalanced with one another (the interband relaxation processes have a typically ns characteristic time τ_n). (c) Preferential collection of a type of charge carrier to each contact after a time of transit τ_D. M1 and M2 are the two contacts, here pictured as metallic, for the holes and the electrons, respectively. BC is the bottom of conduction band, BV is the top of valence band, LUMO is the lowest unoccupied molecular orbital, HOMO is the highest occupied molecular orbital; they play a similar role in solids and molecules, respectively.**

▼ **FIG. 2: Recoverable optimal free energy μ by an absorbed photon, *i.e.*, at the maximum electric power extraction (ordinate, left axis), according to both the photon energy (abscissa axis) and the incident photon flux (different curves). The blue curve corresponds to a 6000 K black body spectrum, the red curve to the terrestrial solar intensity, and the black curve with that of solar flux above the atmosphere. Green curves: the photons fluxes on a log scale (right axis) for the same spectra.**



Very high-efficiency pathways

The possible strategies are along three main directions, all having ultimately conversion efficiencies close to 85 %.

1. *The 'photonic' devices:* if all solar energy were concentrated in a narrow spectral band, the current devices would already be able to convert somewhat over 50%. One can thus try to adapt the incident spectrum to one or more photodiodes. The new requirements translate into optical properties of materials.
2. *Optimised absorption materials:* materials having intermediate electronic levels serving as "scale for electrons" or materials allowing the generation of several electron-hole pairs by sufficiently energetic photons . These requirements involve the electronic structure of materials.
3. *Heat engines* in which the absorption of light leads to the production of heat that can still be converted into electric output. In this last case, one needs to look closely at the thermal and "phononic" properties of the solids considered.

I- Photonic devices

Here, the difficult task is either to sort photons to be sent to junctions adapted to the corresponding part of the spectrum (multi-junctions), or to change their energy so as to lead to a "bunched" distribution, before being recovered each time by a standard diode adapted to this narrowed spectrum.

a. Multi-junctions

notes

[1] When E_{fn}-E_{fp} becomes close to E_g, one reaches population inversion between electrons and holes, and stimulated emission of radiation opposes a further increase in qV.

[2] In most cases, $E_f = E_f° + kT.log[n]$, where n is the concentration of electrons of the group of energy levels in (quasi-) equilibrium and $E_f°$ the free energy of the standard state, similar to that of the chemical potential of a perfect gas.

[3] The maximum concentration factor is 4π divided by the solid angle of the sun, *i.e.*, when the cell can only see the sun. At higher concentration factors, the focal point would have a higher radiation temperature than the source, which is thermodynamically impossible.

[4] If not, one could reversibly transport heat of a cold body towards a hot body, and we would have a perpetual motion machine.

In a traditional device, the photons whose energy conversion is most effective are those whose energy is just above the threshold of absorption (energy gap E_g). For those, outputs of about 60 % are reached in experiments, rather close to expectations (fig. 2). The use of several different cells materials, each one with a gap optimised for a different part of the solar spectrum, makes it possible to increase the output (see box). For a given number of cells and an incident spectrum, there is a best choice for the gaps giving the highest output [2]: for example, for three cells under maximum concentration, the maximum theoretical yield is 63 % (49 % without concentration). These devices exist, and achieve outputs of ~43 % (under concentration) [3]. They involve very advanced fabrication technology, but represent the first actual devices with very high efficiency potential. The highest efficiencies were obtained with structures based on stacks of epitaxial III-V compounds. Yet, it has to be realized that the incremental gain in power from the addition of a cell in a stack including N junctions, varies like $1/N^2$. If one takes into account the induced losses (electrical and optical), the expected net gain from another cell is close to zero after the 4th cell.

b. Optical converters

Alternatively, one could change the wavelength of the photons before they reach the photodiode, to obtain a narrower spectrum. In the approach 'photon addition', the photons whose energy is too weak to be used directly by a photodiode could be converted by nonlinear optics into a lower number of photons of larger energy. The main results on this topic have been obtained with materials in which infrared radiation is absorbed by several ions of a rare earth and its energy transferred to another lanthanide, able to emit effectively at close to double frequency [4]. So far, approximately 16 % of the absorbed photon energy in the infrared was actually converted into photons of twice the energy.

Another principle, 'photon cutting' consists in absorbing photons of high energy in a luminescent converter to emit several photons of lower energy, to increase the current output of the photodiode. Fluorescent converters such as YF_3:Pr or $LiGdF_4$:Eu have been proposed but are only efficient with UV light.

II- Optimized absorption mechanisms

a. Intermediate levels devices

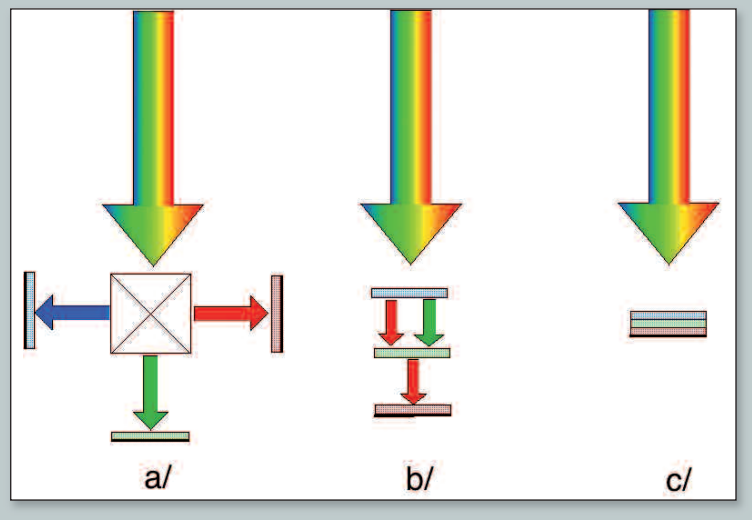
In addition to the transitions from the valence band to the conduction band, which take place in the semiconductors under the effect of irradiation, semiconductors can absorb photons of even lower energy via intermediate levels located in the forbidden band, which play the role of a 'ladder for electrons' (fig. 3 b) [5]. Such a device would be similar to a multi-junction with respect to efficiency, but with the simplicity of a simple junction. The main issue is achieving a strong absorption of the intermediate levels without excessively increasing the rate of non-radiative recombination. There are many ways of obtaining intermediate levels or bands like, for example, by the introduction of extended defects or impurities, or of a superlattice of quantum dots. Other intermediate level systems have appeared more recently: ferromagnetic semiconductor compounds, of the type of GaAs:Mn, could present reduced non-radiative decay , because of the selection rules on the spin which could slow down some recombination processes [6].

b. 'Scintillators' materials

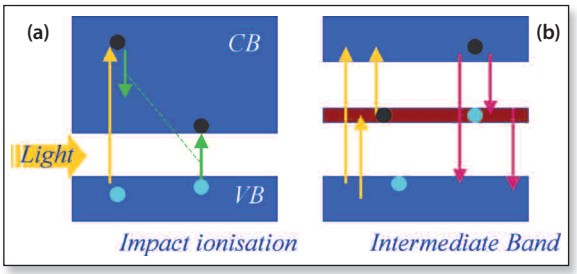
The absorption of photons having energy more than twice that of the gap makes it possible to consider other mechanisms, where the excess energy can be used to create a second electron-hole pair. This phenomenon is called 'impact ionisation' (fig. 3a). The outputs of devices with impact ionisation can have practical interest, provided that the process is effective in the vicinity of the physical threshold (~ 2 E_g). Work at the Max Planck Institute of Stuttgart predicted that the alloys Si-Ge could show a measurable effect. But this was found to be lower

Principle of multi-spectral conversion (triple junction)

a) An optical device separates sunlight by means of filters in three beams "blue", "green" and "red", which are converted by three cells whose band gaps were adapted for these three spectral bands. One can simplify the device as indicated in b) noticing that the "blue" cell does not absorb the wavelengths higher than its threshold of absorption. It can thus be used as filter for "green" and "red" cells. In the same way, the "green" cell lets the "red" beam pass. It is necessary, of course, that the substrates of the first two cells are transparent. Finally, in c) a transparent electrical contact between the cells is realized.



One can achieve this stack by deposition of the various cells on the same substrate. To avoid creation of a reverse diode at the interface between two cells (a diode p-n if diodes n-p are piled up), one connects them by a tunnel junction. In case c) the cells are connected in series, whereas in the cases a) or b) one remains free to use the electricity produced in the most effective way.



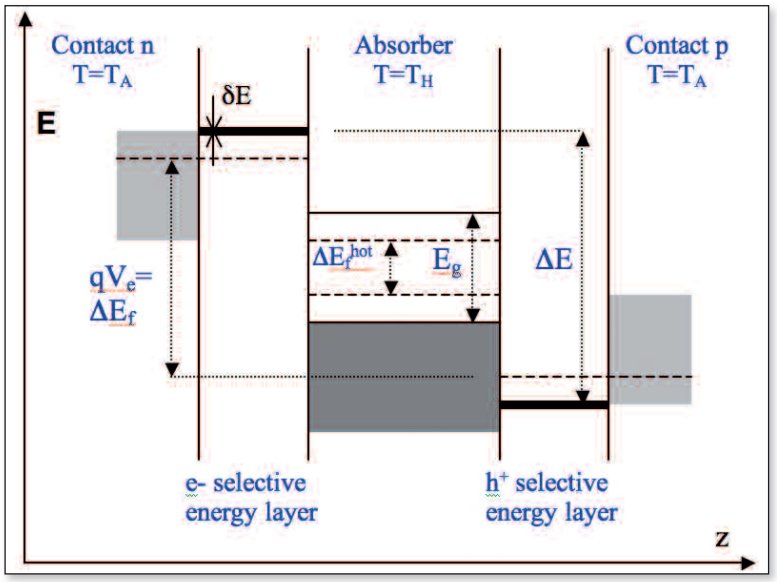
▲ **FIG. 3:** Energy band diagram showing potentially improved carrier compared to the standard case. (a) Impact ionisation enables transfer excess of energy from a carrier to an electron which becomes promoted from the valence band (VB) to the conduction band (CB). (b) An intermediate band allows a better absorption of the solar spectrum. The processes of generation are in yellow and those of recombination are pink.

than 1 % of the output power of cells made of this material. High values of impact ionization have so far been observed only for energies of photons higher than 3 E_g [7].

III- 'Heat engines': hot-carriers solar cells

The carriers generated in the absorber are not thermalised instantaneously with the network at temperature T_A, but form in a transitory way a hot gas of electrons and holes: their distribution corresponds to a temperature $T_H > T_A$. If these carriers can be collected quickly via selective energy levels (fig. 4), the heat flow through the contacts is minimal and the kinetic energy conversion of hot gas into electrical potential energy is optimal [8]. Calculations of the limit of output give values very close to those obtained with a multi-junction device containing an infinite number of cells, each one adapted to a fraction of the spectrum, and this for a system of a much simpler concept. It thus acts, to some extent, as the ultimate device of solar transformation energy. No cell with hot carriers was built yet. However, experiments showed that hot carriers thermalisation rates can be reduced under strong excitation in nanostructures to the point that conversion efficiencies above 50 % under concentration are possible [9]. These outputs are sensitive to the energy width of the contacts beyond some meV, because the latter introduce a thermal loss by transfer of heat. But more than decreasing the thermalisation rate, the practical realization of selective contacts is likely to be the delicate point in the fabrication of these devices.

▼ **FIG. 4:** Energy band diagram of a hot-carriers cell. The solar photons are absorbed in the central part where a gas of hot electrons is formed. The internal free energy available (at T_H) is ΔE_f^{hot}. Their excess of kinetic energy enables them to be collected at an energy higher than that of the edge of the conduction band (for the electrons) or valence band (for the holes): the energy per pair ΔE can be significantly larger than E_g. The selectivity in energy (given by δE, the energy width) of the contact is enabling minimal heat transfer of hot carriers to the contacts.



Conclusion

Will we find systems radically different from diodes for high performance photovoltaic conversion? There are in any case a great number of possibilities to achieve that. In the short run, multi-junction devices should demonstrate significant progress. They may even have a significant impact on the production of photovoltaic electricity, by using solar tracking and concentration, on a somewhat longer term. Finally, later on, cells with intermediate levels or hot carriers, which raise the greatest scientific and technological challenges, could enable us to approach the ultimate performances. Thanks to the discovery of new materials resulting, for instance, from nanotechnologies, this possibility is getting closer every day. ■

About the author

J.F. Guillemoles is Research Director at the Centre National de la Recherche Scientifique (CNRS) and deputy director of IRDEP, a joint CNRS-EDF-ParisTech R&D Institute.

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