## Efficiency Enhancement in Photovoltaic-Thermoelectric Hybrid Cells

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#### Abstract

The potential of advanced approaches to photovoltaic energy conversion have been evaluated mostly by considering idealized systems (radiative recombination limit, infinite carrier mobility, optimal absorption, lossless contacts). How can these stringent constraints be relaxed without loosing too much of the benefits proposed? How can real systems perform better, while keeping the unit costs within those of today's technologies? In this work, we consider the effect of finite mobility of the charge carriers and finite heat conductivity on the current voltage characteristics and efficiency limit of a solar cell. We find in fact an increase of the efficiency of a solar cell beyond the Shockley-Queisser{limit [1]. The additional driving force for this gain is the temperature gradient between the optically active region of the cell and its surroundings,due to the fast relaxation of the excited electron-hole pairs. The effect is small in conventional solar cells[2], but can be increased by insertion of a lower band gap material into the optically active region, due to an enhancement of the figure of merit. This was recently shown to be due to the repulsion of thermal phonons from the heterostructure interfaces [3]. Here, we consider the total efficiency limit of a combined photovoltaic-thermoelectric cell. It is explored how the insertion of heterostructures and disorder does influence the performance of such hybrid cells, and if this can yield a bridge towards practical implementation of a real 3rd generation solar cell.

## 1.Introduction

As solar flux is composed of a broad band radiation it is difficult to convert it efficiently into electrical power in a single device. There are theoretically a number of possibilities [4] to reach conversion efficiencies beyond the Schockley limit of a single band gap device, including the use of tandem systems (Henry, 1980 [5]), fluorescent mirrors (Gibart, 1995 [6]), impact ionization (Kolodinsky, 1994 [7]), impurity level systems (Corkish, 1993 [8]), intermediate bands (Kettemann,Guillemoles 1995 [9] and Luque, 1997 [10]), hot electrons (Ross 1982 [11]). The main question remaining is about their practical implementation in real devices. Up to date, tandem systems have been the only ones to demonstrate efficiencies beyond the Schockley limit [1], practically. But this is done through a considerable complexity of device design and at the price of a large sensitivity of the efficiency to the illumination spectrum. In the following, we turn to the investigation of another scheme. One can think of using the thermal energy generated from the relaxation of photogenerated carriers excess energy or from nonradiative recombination at different stages of the thermal equilibration: before equilibration with the lattice (hot carriers), before the cell becomes isothermal or before it equilibrates with the surrounding (thermoelectric, thermoionics, thermophotonics).

### 2. Thermoelectric Efficiency Enhancement

A temperature gradient in the cell gives rise to the thermoelectrical effect, the occurrence of a voltage opposing a temperature gradient in a device, which results in a current when the electrical circuit is closed. The excited charge carriers which are created in the optically active region of the semiconductor can be transported to the contacts driven by the temperature gradient between that hot region and its colder surroundings. When the excited, hot electrons are transported to the contacts before they can equilibrate with the lattice, this constitutes a realisation of the hot electron solar cell [11,12].

More realistically, the electrons will relax in the optically active region, emitting with their excess energy phonons. Thereby, the local lattice temperature is increased to  $T_H$ . As a result, the thermoelectric force due to the temperature gradient in the cell enhances the output voltage as shown in Fig. 1. The efficiency

of semiconductor thermoelements which turn temperature gradients into electrical current is limited by the so called figure of merit T Z = T S<sup>2</sup>  $\sigma/\kappa$  q<sup>2</sup> with the thermopower S, the conductivity  $\sigma$ , and thermal conductivity  $\kappa$  [13]. The optimum efficiency of a thermoelement, as defined by the maximal ratio of the output electrical power and the thermal heat transfer rate, is given by

# $\eta = \eta_C ((1 + Z (T + T_H)/2)^{1/2} - 1)/((1 + Z (T + T_H)/2)^{1/2} + T/T_H))$

where  $\eta_C = (T_H - T)/T_H$  is the Carnot efficiency of a heat engine, where  $T_H$  is the higher temperature than the temperature of the surroundings, T. Thus, it is limited by the Carnot efficiency  $\eta_C$ , in the limit of infinite figure of merit ZT. Presently, there is a strong research effort to find materials with improved figure of merit T Z, requiring to maximise the thermopower and the electrical conductivity and minimizing at the same time the thermal conductivity, in order to increase the efficiency of thermoelements substantially. Thin-film thermoelectric devices with high room-temperature figures of 2.4 for p-type Bi2Te3/Sb2Te3 superlattice devices have been reported in [14].



Figure 1: (left) The band diagram of a p-n-solar cell with a higher temperature  $T_H$  in the optically active region than the temperature T of surroundings. The quasi-Fermi levels of electrons and holes are shown

as dashed lines. Their difference defines the voltage which is at the contacts, V, larger than at the p-ninterface,  $V_H$  due to the themoelectrical effect. (right) The efficiency limit of a single band gap solar cell as combined with a thermoelectrical element as function of the band gap  $E_G$  and the cell temperature  $T_H$ .

It has recently been shown that the efficiency of single gap solar cells can indeed be increased beyond the Shockley-Queisser limit due to the temperature gradients inside the cell. However, because of the smallness of the realistic temperature gradients the efficiency enhancement was found not to exceed 1 %, even under strong concentration of sunlight [10]. It might therefore be of interest to combine solar cells with thermoelements to reach a larger overall efficiency. Figure 1 (left) shows the limiting efficiency as function of the band gap  $E_G$  in eV and the temperature  $T_{H-}$ , as obtained by optimising the total efficiency of the combined photovoltaic-thermoelectric cell.

Taking into account the temperature gradients, there is furthermore an enhancement of current and output voltage due to thermionic emission from the optically active region[2], if a semiconductor with a lower band gap than the emitter and basis is inserted there [15]. In summary, the challenge in making efficient use of the themoelectrical effect is to find material systems with an ideal ratio of electrical to thermal conductivity (thereby approaching the Carnot conversion efficiency). Heterostructures and nanopourous systems have been shown to be advantageous to this end.

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