Technical University of Denmark

Emission and Absorption Entropy Generation in Semiconductors

Reck-Nielsen, Kasper; Varpula, Aapo ; Prunnila, Mika ; Hansen, Ole

Published in:
Proceedings of the 28th European Photovoltaic Solar Energy Conference and Exhibition

Publication date:
2013

EMISSION AND ABSORPTION ENTROPY GENERATION IN SEMICONDUCTORS

Kasper Reck[1], Aapo Varpula[3], Mika Prunnila[3], and Ole Hansen[1,2]
[1] DTU Nanotech, Technical University of Denmark, Ørsteds Plads, DK-2800 Kgs. Lyngby, Denmark.
[2] CINF, Technical University of Denmark, Ørsteds Plads, DK-2800 Kgs. Lyngby, Denmark.
[3] VTT Technical Research Centre of Finland, P. O. Box 1000, FI-02044 VTT, Espoo, Finland.

ABSTRACT: While emission and absorption entropy generation is well known in black bodies, it has not previously been studied in semiconductors, even though semiconductors are widely used for solar light absorption in modern solar cells [1]. We present an analysis of the entropy generation in semiconductor materials due to emission and absorption of electromagnetic radiation. It is shown that the emission and absorption entropy generation reduces the fundamental limit on the efficiency of any semiconductor solar cell even further than the Landsberg limit. The results are derived from purely thermodynamical considerations and are thus of general validity. A modified Landsberg efficiency and numerical results are given.
Keywords: Fundamentals, Modelling, Performance

1 BACKGROUND

When designing and optimizing high efficiency solar cells it is often valuable to be able to identify efficiency limiting mechanisms by considering an idealized efficiency model of the cell. Such efficiency limit models can be specific to a given design, as e.g the Shockley-Queisser limit, or fundamental, as e.g. the Carnot limit. While design specific limits are relevant for optimizing a certain type of solar cells, fundamental limits allow for a better understanding of solar cells in general and possibly also new solar cell designs. Fundamental limits on the maximum efficiency are often calculated by application of thermodynamical methods, i.e. energy and entropy considerations. A widely accepted fundamental limit for any solar cell design is the Landsberg limit [2], which considers simply the sun and a black body absorber in a thermal reservoir. The unavoidable entropy generation due to absorption and emission of radiation in the black body absorber effectively reduces the maximum efficiency from 93.3% to 85.4% or by 7.9 percent point. The emission and absorption entropy generation flux for black bodies are given by [3]

$$\dot{S}_{\mathrm{gen,emi}} = \frac{1}{3}\frac{\dot{E}_c}{T_c}$$

and

$$\dot{S}_{\mathrm{gen,abs}} = \dot{E}_s\left(\frac{1}{T_c} - \frac{4}{3}\frac{1}{T_s}\right)$$

respectively, where $\dot{E}_c$ is the radiative energy flux from the cell, T_c is the temperature of the cell, $\dot{E}_s$ is the energy flux from the sun and T_s is the temperature of the sun. Clearly, the total entropy generation terms are only zero if $T_c = T_s$. We derive the entropy generation flux expressions for the more general case of semiconductor bodies and apply the results to calculate the Landsberg limit for semiconductor solar cells. In the case of a black body/semiconductor system (e.g. the sun and a solar cell), the total emission and absorption entropy generation in the semiconductor is shown to approximately equal

$$\dot{S}_{\mathrm{gen}} \cong \dot{E}_{s,\mathrm{abs}}\left(\frac{1}{T_c} - \frac{1}{T_s}\right) - \frac{\mu_c}{T_c}\dot{N}_{s,\mathrm{abs}} + k_{\mathrm{B}}\left(\dot{N}_c - \dot{N}_{s,\mathrm{abs}}\right), \quad (1)$$

where $\dot{E}_{s,\mathrm{abs}}$ and $\dot{N}_{s,\mathrm{abs}}$ are the solar flux magnitudes for photons above the band gap of the semiconductor, $\dot{N}_c$ is the photon radiation flux of the cell, μ_c is the chemical potential of the cell and k_{B} is Boltzmann's constant.

2 ANALYSIS

Consider two semiconductors, a and b, at temperatures T_a and T_b, with band gaps E_{g_a} and E_{g_b} and electron-hole pair chemical potentials μ_a and μ_b, respectively. It is assumed that the band gaps are direct with an absorptivity of unity above the band gap, that thermalization of generated electron-hole pairs is rapid, and that only radiative recombination is present. For simplicity, the band gaps are assumed equal, and thus all incident photons may be absorbed. If this assumption is not fulfilled, the resulting efficiency will be further reduced.

Since only radiative recombination is allowed the total number of photons and electron-hole pairs is conserved and then the electron-hole pair fluxes $\dot{N}_{\mathrm{eh}_a}$ and $\dot{N}_{\mathrm{eh}_b}$ are related to the photon radiation fluxes $\dot{N}_a$ and $\dot{N}_b$ as

$$\dot{N}_{\mathrm{eh}_a} = -\dot{N}_{\mathrm{eh}_b} = \dot{N}_a - \dot{N}_b, \quad (2)$$

where all flux magnitudes inside the semiconductors are positive in a direction towards the emitting surface as illustrated in Fig. 1.

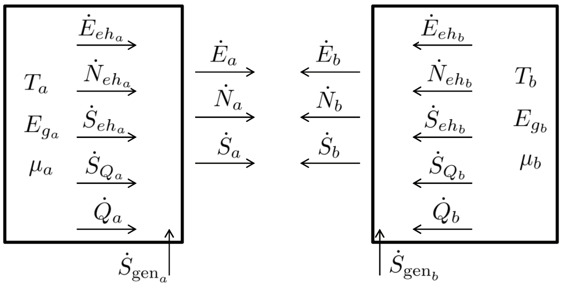

Figure 1: Schematic of the setup with two radiating semiconductors. Flux magnitudes inside the semiconductors are positive in the direction towards the emitting surface.

Energy conservation applied to semiconductor a in steady state requires that the emitted photon energy flux $\dot{E}_a$ equals the absorbed photon energy flux $\dot{E}_b$ plus the electron-hole pair energy flux $\dot{E}_{\mathrm{eh},a}$ and the heat current $\dot{Q}_a$, i.e.

$$\dot{E}_a - \dot{E}_b = \dot{E}_{\mathrm{eh},a} + \dot{Q}_a. \tag{3}$$

Similarly, the entropy fluxes fulfil

$$\dot{S}_a - \dot{S}_b = \dot{S}_{\mathrm{eh}_a} + \dot{S}_{Q_a} + \dot{S}_{\mathrm{gen}_a}, \tag{4}$$

where $\dot{S}_a$ and $\dot{S}_b$ are the entropy fluxes associated with the photons emitted from the two semiconductors, $\dot{S}_{\mathrm{eh}_a}$ is the entropy flux carried by the electron hole pairs, while $\dot{S}_{Q_a} = \dot{Q}_a / T_a$ is the entropy flux due to the heat flow, and finally, $\dot{S}_{\mathrm{gen}_a}$ is the (irreversible) entropy flux generated in semiconductor a. In Eq. 4 we may solve for $\dot{S}_{\mathrm{gen}_a}$ and use Eq. 3 to eliminate the waste heat flow

$$\dot{S}_{\mathrm{gen}_a} = \dot{S}_a - \dot{S}_b - \dot{S}_{\mathrm{eh},a} + \frac{\dot{E}_b + \dot{E}_{\mathrm{eh},a} - \dot{E}_a}{T_a} \tag{5}$$
$$= \frac{\left(\dot{E}_b - T_a\dot{S}_a\right) + \left(\dot{E}_{\mathrm{eh},a} - T_a\dot{S}_{\mathrm{eh},a}\right) - \left(\dot{E}_a - T_a\dot{S}_a\right)}{T_a}.$$

To proceed further expressions relating the fluxes are necessary. The photon flux $\dot{N}_i$ and photon energy flux $\dot{E}_i$ from each semiconductor are given by [4, 5]

$$\dot{N}_i = C_i \int_{E_{g_i}}^{\infty} \frac{\varepsilon^2}{\exp\frac{\varepsilon - \mu_i}{k_\mathrm{B} T_i} - 1} \mathrm{d}\varepsilon \tag{6a}$$

and

$$\dot{E}_i = C_i \int_{E_{g_i}}^{\infty} \frac{\varepsilon^3}{\exp\frac{\varepsilon - \mu_i}{k_\mathrm{B} T_i} - 1} \mathrm{d}\varepsilon, \tag{6b}$$

respectively, where $C_i = 2\xi_i / (h^3 c^2)$ here h is Planck's constant, c is the speed of light in vacuum, ξ_i is the etendue, and $i \in [a, b]$. The corresponding entropy flux is [4, 5]

$$\dot{S}_i = \frac{\dot{E}_i - \mu_i \dot{N}_i}{T_i} - k_B C_i \int_{E_{g_i}}^{\infty} \varepsilon^2 \ln\left[1 - \exp\left(-\frac{\varepsilon - \mu_i}{k_B T_i}\right)\right] \mathrm{d}\varepsilon \tag{7}$$
$$\equiv \frac{\dot{E}_i - \mu_i \dot{N}_i}{T_i} + \Delta\dot{S}_i,$$

where the shorthand $\Delta\dot{S}_i$ is introduced to represent the integral. The electron-hole pair energy flux $\dot{E}_{\mathrm{eh}_i}$ and entropy flux $\dot{S}_{\mathrm{eh}_i}$ are related to the electron-hole pair flux $\dot{N}_{\mathrm{eh}_i}$ by [5]

$$\dot{E}_{\mathrm{eh}_i} = \left(E_{g_i} + 4k_\mathrm{B} T_i\right) \dot{N}_{\mathrm{eh}_i} \tag{8a}$$

and

$$\dot{S}_{\mathrm{eh}_i} = \frac{E_{g_i} - \mu_i + 4k_\mathrm{B} T_i}{T_i} \dot{N}_{\mathrm{eh}_i} \tag{8b}$$

since the faster electrons and holes contribute more to the energy flux than the slower particles; note, the mean electron-hole pair energy is $E_{g_i} + 3k_\mathrm{B} T_i$ and the average entropy per electron hole pair is $\left(E_{g_i} - \mu_i + 5k_\mathrm{B} T_i\right) / T_i$.

3 PURE EMISSION AND PURE ABSORPTION

In pure emission from semiconductor a we take $\dot{S}_b = 0$ and $\dot{E}_b = 0$, and then the entropy flux generated in pure emission is $\dot{S}_{\mathrm{genE}_a}$

$$\dot{S}_{\mathrm{genE}_a} = \dot{S}_a - \dot{S}_{\mathrm{eh}_a} + \frac{\dot{E}_{\mathrm{eh}_a} - \dot{E}_a}{T_a}$$
$$= \mu_a \left(\dot{N}_{\mathrm{eh}_a} - \dot{N}_a\right) + \Delta\dot{S}_a = \Delta\dot{S}_a \cong k_\mathrm{B} \dot{N}_a,$$

where we have used that in this case $\dot{N}_{\mathrm{eh}_a} = \dot{N}_a$. The approximation is valid at sufficiently large band gap and sufficiently small chemical potential, while a blackbody would give $\dot{S}^{\mathrm{BB}}_{\mathrm{genE}_a} = \frac{1}{3} \dot{E}_a / T_a$ as it should.

In the case of pure absorption in semiconductor a we take $\dot{E}_a = 0$ and $\dot{S}_a = 0$ in Eq. 5 to get the generated entropy flux due to absorption

$$\dot{S}_{\mathrm{genA}_a} = -\dot{S}_b - \dot{S}_{\mathrm{eh},a} + \left(\dot{E}_b + \dot{E}_{\mathrm{eh},a}\right) / T_a$$

$$= \dot{E}_b\left(\frac{1}{T_a}-\frac{1}{T_b}\right)+\dot{N}_b\left(\frac{\mu_b}{T_b}-\frac{\mu_a}{T_a}\right)-\Delta\dot{S}_b$$
$$\approx \dot{E}_b\left(\frac{1}{T_a}-\frac{1}{T_b}\right)+\dot{N}_b\left(\frac{\mu_b}{T_b}-\frac{\mu_a}{T_a}\right)-k_\mathrm{B}\dot{N}_b, \quad (9)$$

where the approximation is valid if the band gap of semiconductor b is sufficiently large and the chemical potential sufficiently small; in the case of blackbodies the last term becomes $-\frac{1}{3}\dot{E}_b/T_b$, while the chemical potential term vanish, and then $\dot{S}_{\mathrm{genA}_a}$ reduces to $\dot{S}^{\mathrm{BB}}_{\mathrm{genA}_a} = \dot{E}_b/T_a - \frac{4}{3}\dot{E}_b/T_b$ as it should.

3.1 Emission and Absorption Combined

The generated entropy flux in semiconductor a when emission and absorption is combined gives

$$\dot{S}_{\mathrm{gen}_a} = \dot{E}_b\left(\frac{1}{T_a}-\frac{1}{T_b}\right)+\dot{N}_b\left(\frac{\mu_b}{T_b}-\frac{\mu_a}{T_a}\right)+\Delta\dot{S}_a-\Delta\dot{S}_b$$
$$\approx \dot{E}_b\left(\frac{1}{T_a}-\frac{1}{T_b}\right)+\dot{N}_b\left(\frac{\mu_b}{T_b}-\frac{\mu_a}{T_a}\right)+k_\mathrm{B}\left(\dot{N}_a-\dot{N}_b\right), \quad (10)$$

which is zero in quasi-equilibrium for two identical semiconductors at identical temperatures and identical chemical potentials. The corresponding expression for the generated entropy flux $\dot{S}_{\mathrm{gen}_b}$ in semiconductor b is obtained by interchanging subscripts a and b. It follows that the total generated entropy flux in the two semiconductors is

$$\dot{S}_{\mathrm{gen}} = \dot{S}_{\mathrm{gen}_a} + \dot{S}_{\mathrm{gen}_b}$$
$$= \left(\dot{E}_b-\dot{E}_a\right)\left(\frac{1}{T_a}-\frac{1}{T_b}\right)+\left(\dot{N}_a-\dot{N}_b\right)\left(\frac{\mu_a}{T_a}-\frac{\mu_b}{T_b}\right).$$

If body b is now the sun, while body a is a semiconductor, the entropy generation in the semiconductor is approximately

$$\dot{S}_{\mathrm{gen}_a} \cong \dot{E}_{s,\mathrm{abs}}\left(\frac{1}{T_a}-\frac{1}{T_s}\right)-\frac{\mu_a}{T_a}\dot{N}_{s,\mathrm{abs}}+k_\mathrm{B}\left(\dot{N}_a-\dot{N}_{s,\mathrm{abs}}\right).$$
(11)

where $\dot{E}_{s,\mathrm{abs}}$, $\dot{S}_{s,\mathrm{abs}}$ and $\dot{N}_{s,\mathrm{abs}}$ are the solar flux magnitudes for photons above the band gap of the semiconductor, while the total solar flux magnitudes are $\dot{E}_s$, $\dot{S}_s$ and $\dot{N}_s$. The ratio $\eta_{\mathrm{abs}} = \dot{E}_{s,\mathrm{abs}}/\dot{E}_s$ is the band gap dependent absorber efficiency. The approximation is due to the evaluation of the integrals ($\Delta\dot{S}_i$) in Eq. 10.

4 RESULTS

If body b is the sun and body a the solar cell then the maximum efficiency as given by Landsberg is [2]

$$\eta = \left(1-\frac{\dot{E}_a}{\dot{E}_b}\right)+T_a\frac{\dot{S}_a-\dot{S}_b-\dot{\sigma}_{\mathrm{int}}}{\dot{E}_b}, \quad (12)$$

where $\dot{\sigma}_{\mathrm{int}}$ is the internal entropy generation and T_a is the ambient temperature. This however should be compensated for the absorption characteristics of the semiconductor, such that the corrected efficiency becomes

$$\eta = \eta_{\mathrm{abs}}\left[\left(1-\frac{\dot{E}_a}{\dot{E}_{s,\mathrm{abs}}}\right)+T_a\frac{\dot{S}_a-\dot{S}_{s,\mathrm{abs}}-\dot{\sigma}_{\mathrm{int}}}{\dot{E}_{s,\mathrm{abs}}}\right], \quad (13)$$

where the internal entropy generation $\dot{\sigma}_{\mathrm{int}}$ as a minimum is given as Eq. 11. The useful power is $-\mu_a\dot{N}_{\mathrm{eh}_a}$ (the minus sign is due to the sign convention for the flux magnitudes) and thus an alternative efficiency expression is

$$\eta = \eta_{\mathrm{abs}}\frac{-\mu_a\dot{N}_{\mathrm{eh}_a}}{\dot{E}_{s,\mathrm{abs}}}, \quad (14)$$

which is in agreement with the modified Landsberg equation, which is easily proven by insertion of Eq. 5 in the modified Landsberg equation. Eq. 14 can be written in closed form, i.e. without the integrals implicitly represented by $\dot{N}_{\mathrm{eh}_a}$, using polylogarithms and Stefan-Boltzmann's law, i.e.

$$\eta = \mu_a\left(\frac{30\xi(3)}{\pi^4}-\frac{C}{\sigma T_s^{\,4}\Omega}\left(2\,\mathrm{Li}_3(\kappa_a)T_a^{\,3}k_b^{\,3}\right.\right.$$
$$\left.\left.+2\,\mathrm{Li}_2(\kappa_a)T_a^{\,2}k_b^{\,2}E_g+\mathrm{Li}_1(\kappa_a)T_a k_b E_g^{\,2}\right)\right)$$

where ξ is the Riemann zeta function, σ is the Stefan-Boltzmann constant, Ω is the reciprocal concentration factor, Li_n is the polylogarithm of order n and

$$\kappa_a = \exp\left(-\frac{E_g-\mu}{k_b T_a}\right)$$

The total generation entropy flux for a semiconductor solar cell at $T_a = 298$ K and $T_a = 373$ K is shown in Fig. 2 as function of band gap and the ratio of chemical potential to band gap.

For comparison, the average internal entropy flux for the band gaps and chemical potentials considered here is $\sigma_{\mathrm{int}} = 2.2$ J/m²sK while the corresponding black body radiative entropy is $\dot{S}_{a,BB} = 2$ J/m²sK.

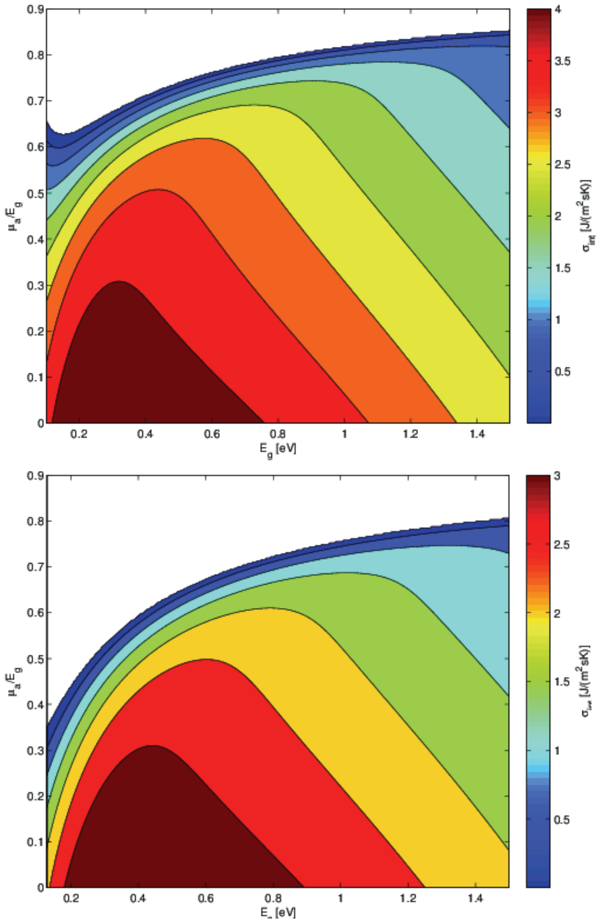

Figure 2: The total generation entropy for a solar cell at 298 K (top) and 373 K (bottom), respectively. The band gap ranges from 4 to 1.5 eV. The internal entropy generation flux is in general larger or comparable to the radiative entropy flux. Notice the forbidden (white) area at high chemical potential.

Thus internal entropy generation contributes significantly to the total entropy flux. The white areas in the plots correspond to negative internal entropy generation and are thus not allowed according to the second law of thermodynamics.

The curves of zero entropy generation are plotted in Fig. 3 for different temperatures of body *a*. Differences between band gap and chemical potential below these curves are not allowed. It is seen that as the temperature of body *a* is increased, the minimum allowable difference between band gap and chemical potential is increased.

4 CONCLUSION

In this paper expressions for the fundamental and unavoidable internal entropy generation in semiconductor solar cells due to emission and absorption of electromagnetic radiation has been derived. These expressions are of general validity and includes black body internal entropy generation as a special case. A modified Landsberg efficiency is given along with numerical calculations of the total entropy generation flux. From the numerical calculations it is found that the (negative) contribution to solar cell efficiency from

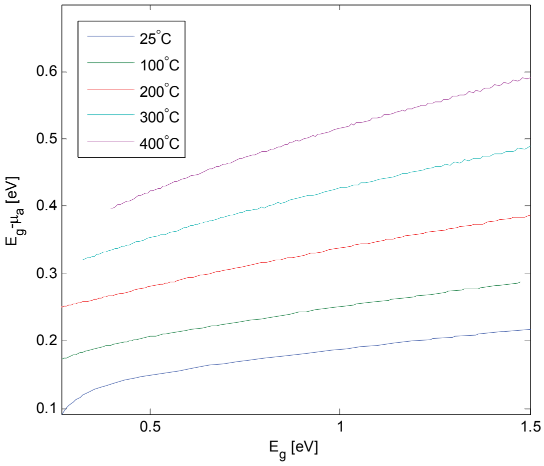

Figure 3: Curves of zero entropy flux generation at different temperatures of body *a*. Points below the curves are not allowed. As the temperature is increased the minimum allowable difference between band gap and chemical potential is increased.

internal entropy generation is larger or comparable to the radiative entropy contribution from a black body at the same temperature and the internal entropy generation is thus of significant importance for the overall efficiency. Finally, it is found that some combinations of band gap and chemical potential yields negative internal entropy generation and are thus forbidden according to the second law of thermodynamics.

4 ACKNOWLEDGEMENTS

This work has been financially supported by Nordic Energy Research (project HEISEC) and by The Danish National Research Foundation's Center for Individual Nanoparticle Functionality-CINF (DNRF54).

REFERENCES

[1] T. Saga, "Advances in crystalline silicon solar cell technology for industrial mass production", NPG Asia Materials, vol. 2, no. 3, p. 96-–102, 2010

[2] P. T. Landsberg and G. Tonge, "Thermodynamic energy conversion efficiencies", Journal of Applied Physics, vol. 51, no. 7, p. R1-–R20, 1980

[3] A. D. Vos and H. Pauwels, "Comment on a thermodynamical paradox presented by P. Wurfel", Journal of Physics C: Solid State Physics, vol. 16, no. 36, p. 6897-–6909, 1983.

[4] M. A. Green, "Third generation photovoltaics", Springer-Verlag Berlin Heidelberg, 2003

[5] J. E. Parrott, "Thermodynamic theory of transport processes in semiconductors", IEEE Transactions on Electron Devices, vol. 43, no. 5, p. 809-–826, 1996