



HAL
open science

Absorption coefficient and non-equilibrium generalized Planck's law for improved hot carrier photoluminescence spectroscopy

François Gibelli, Laurent Lombez, Jean-Francois Guillemoles

► To cite this version:

François Gibelli, Laurent Lombez, Jean-Francois Guillemoles. Absorption coefficient and non-equilibrium generalized Planck's law for improved hot carrier photoluminescence spectroscopy. 2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC), 2016, Portland, United States. <10.1109/PVSC.2016.7750336>. <hal-02344154>

HAL Id: hal-02344154

<https://centralesupelec.hal.science/hal-02344154v1>

Submitted on 5 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Absorption coefficient and non-equilibrium generalized Planck's law for improved hot carrier photoluminescence spectroscopy.

François Gibelli*[†], Laurent Lombez*^{†‡}, Jean-François Guillemoles*^{†‡}

*IRDEP, 6 quai Watier, 78400 Chatou, France

[†]Next PV LIA, 4-6-1 Komaba, Meguro-ku, Tokyo, Japan

[‡]IPVF, 8 rue de la renaissance, 92160 Antony, France

Abstract—The generalized Planck's law describes the light emitted by a blackbody. In the past this law has been generalized to semiconductors. Whereas Planck's original formulation roots on a same temperature between the body and the emitted photon gas, the generalized expression for semiconductors has been used to describe electron-hole plasmas in non-equilibrium with the lattice. Here we show experimentally how to determine different electron and hole temperatures in non-equilibrium with the photon gas. Since the absorption coefficient varies with the carrier density and is part of the generalized Planck's law, we particularly emphasize the importance of the absorption coefficient in the analysis of hot carrier photoluminescence spectra.

Index Terms—hot carrier solar cells, hot carrier photoluminescence, non-equilibrium generalized Planck's law, non-equilibrium electron and hole distributions

I. INTRODUCTION

The radiation emitted by the blackbody has been generalized to non-blackbodies [1] and applied to semiconductors. This so called generalized Planck's law enables to access the fundamental thermodynamical properties of the carriers, namely their temperature [2] and electrochemical potential [3]. This generalized Planck's law has been widely used to fit hot carrier photoluminescence spectra [4]. However the temperature measured with this method has been defined by Planck as an *emission temperature*[5], which characterizes a body in equilibrium with the radiation that it emits. In the case of hot carriers, the carriers are considered to be hot whereas the lattice of the material remains cold. But it is not clear which carrier heats [6] and the relationship between the measured emission temperature and the corresponding temperatures characterizing each carrier temperature.

II. THEORY & METHOD

A. Non equilibrium generalized Planck's law

The classical expression of the generalized Planck's law writes:

$$I_{PL}(E) = \frac{A(E)E^2}{4\pi^2\hbar^3c^2} \left[\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1 \right]^{-1} \quad (1)$$

where A is the energy dependant absorptivity of the material, E the energy of the emitted photon, k_B the Boltzmann constant, T the emission temperature and $\Delta\mu$ the quasi Fermi level splitting (electrochemical potential difference).

This expression is generally used to linearly fit the experimental data, with an absorptivity measured with a spectrophotometer and considered to be independant from the carrier thermodynamical properties.

In order to see the relationship between the emission temperature and the temperatures of electrons and holes, this law has to be rewritten for non-equilibrium carriers.

This has been done successfully[7], so that the electron and hole thermal non-equilibrium generalized Planck's law for a quantum well structure, considering parabolic bands, writes:

$$I_{PL,QWe}(\hbar\omega) = \frac{A(\hbar\omega)(\hbar\omega)^2}{4\pi^2\hbar^3c^2} \times \left[\exp\left(\frac{1}{k_B} \left(\frac{1}{T_H^e} - \frac{1}{T_H^h}\right) \times \left[\left(\frac{m^e}{m^e + m^h}\right) \left(\frac{E_C}{2} + E_c^i\right) - \left(\frac{m^h}{m^e + m^h}\right) \left(\frac{E_G}{2} + |E_v^j|\right) \right] \right) + \frac{\hbar\omega}{k_B(m^e + m^h)} \left(\frac{m^h}{T_H^e} + \frac{m^e}{T_H^h}\right) - \frac{\mu_H^e}{k_B T_H^e} - \frac{\mu_H^h}{k_B T_H^h} - 1 \right]^{-1} \quad (2)$$

where $\hbar\omega$ is the energy of the emitted photon, $A(\hbar\omega =$ the absorptivity of the material, T_H^e, T_H^h the hot electron and hole temperatures respectively, μ_H^e, μ_H^h the hot electron and hole absolute electrochemical potentials respectively, m^e, m^h the effective mass of electrons in the conduction band and of holes in the valence band and E_C^i, E_V^j the confinement energy of the first conduction and valence levels in the quantum well.

However, this is not sufficient to fit the photoluminescence spectra, especially at high incident photon fluxes.

B. Absorptivity

Indeed, after a first attempt to fit photoluminescence spectra by taking into account the Burstein-Moss effect accounting for the band filling [8], we use a generalized Elliott absorption model[9], [10], [11], [12], [13] for the expression of the absorption coefficient in the non-equilibrium generalized Planck's law. The fit takes into account the band filling effect, as well as exciton screening effects:

$$A(\hbar\omega) = 1 - \exp\left(-\left(A_{lh} \exp\left(-\frac{(\hbar\omega - E_{lh})^2}{\Gamma_{lh}^2}\right) - A_{hh} \exp\left(-\frac{(\hbar\omega - E_{hh})^2}{\Gamma_{hh}^2}\right) - A_C \frac{1}{1 + \exp\left(-\frac{(\hbar\omega - E_C)}{\Gamma_C}\right)} \frac{2}{1 + \exp\left(-2\pi\sqrt{\frac{E_C - E_{lh}}{|\hbar\omega - E_C|}}\right)}\right) (f_V^e - f_C^e)\right) \quad (3)$$

where $A(\hbar\omega)$ is the absorptivity of the material, $A_{lh}, E_{lh}, \Gamma_{lh}$ the amplitude, energy and broadening of the light holes exciton absorption, $A_{hh}, E_{hh}, \Gamma_{hh}$ the amplitude, energy and broadening of the heavy hole exciton absorption, and A_C, E_C, Γ_C the amplitude, energy of the continuum edge and broadening of the unbound excitons, taking into account the Sommerfeld factor for Coulomb interactions. Last the Fermi Dirac distributions of electrons in the valence and conduction

bands respectively f_V^e, f_C^e express the classical band-filling effect.

The expression (3) of the absorptivity is inserted into the non-equilibrium generalized Planck's law given in expression (2). The resulting new expression has enabled us to fit the photoluminescence spectra shown in this work.

C. Experimental method

The sample used for this study is a InGaAsP multi quantum well structure, developed initially for laser research by the laboratory FOTON (Insa, Rennes, France). The sample has 6 wells of 3nm width each, enabling to have a well defined photoluminescence spectrum in the region of the wells. The energy gap of the wells is 0.78 eV at ambient temperature.

The sample has been investigated with a 980 nm laser (1.26eV), generating carriers in both the wells and the barriers. The photoluminescence signal has been recorded by a spatially and spectrally absolutely calibrated hyperspectral setup [14].

III. EXPERIMENTAL RESULTS & DISCUSSION

A. Photoluminescence spectra shape

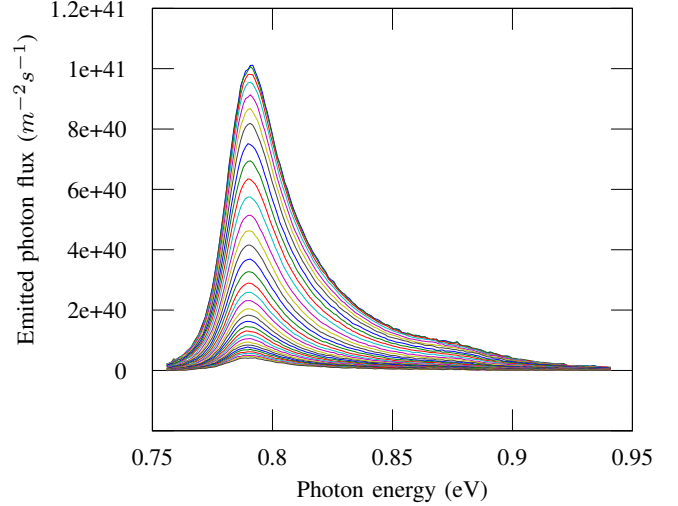
A photoluminescence data set obtained at low incident photon flux has been converted into polar coordinates in order to see the change of the shape of the photoluminescence spectrum with the distance from the laser spot on the sample. As show on Figure 1 (a), the intensity of the photoluminescence spectrum increases for a distance closer to the laser spot. In order to see a possible change of the shape of the spectrum, each photoluminescence spectrum has been normalized according to the value of its peak. The results are shown on Figure 1(b), the shape of the photoluminescence spectrum is changed by going closer to the laser spot. Indeed, the high energy tail (from 0.8eV to 0.95eV) is modified as classically expected in hot carrier photoluminescence[2], but also the low energy tail (0.75eV -0.8eV).

Whereas the change in the low energy tail seems to have a lower magnitude than that in the high energy tail, this change can be only fitted by considering a change of the absorption coefficient, which is possible with the approach presented in this work, with a combination of expressions (2) and (3). The results obtained with this method are discussed below.

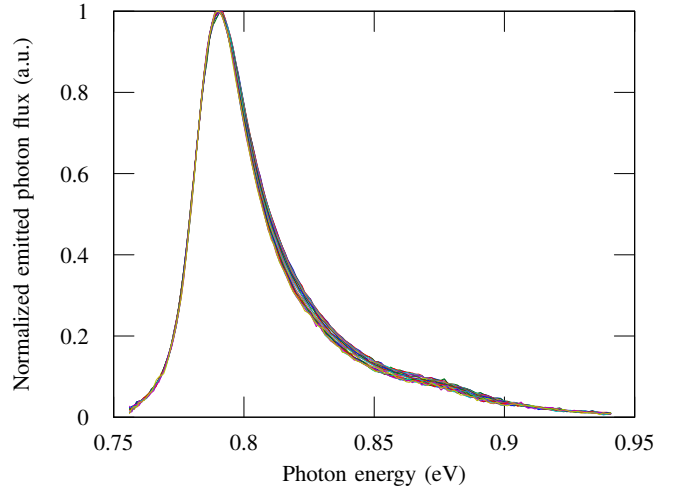
B. Experimental results

Figure 2 show the variation of the carrier temperatures, the electrochemical potential with the distance from the center of the laser beam, from the fit of the hyperspectral photoluminescence data recorded at the lowest incident photon flux.

The temperature of the electrons, in circles on Figure 2 (a), is very close to the emission temperature (triangles on the same figure), obtained with our full spectrum isothermal fit. However the temperature of the electrons is slightly higher than the emission temperature, and the difference increase with the increase of these temperatures. The temperature of the holes, in squares on Figure 2 (a) is lower than both the emission temperature and the electron temperature.



(a) Average spectra in normal scale

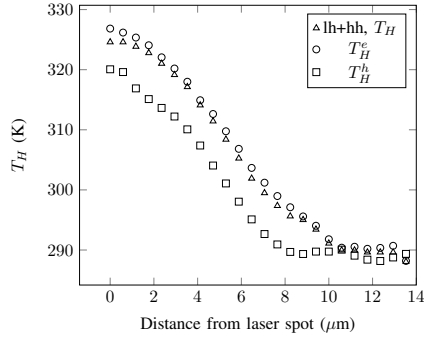


(b) Normalized average spectra

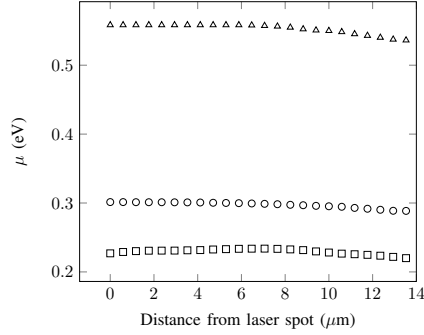
Fig. 1. Average spectra according to the distance of the pixel to the center of the laser beam. The lowest is at 12 μ m and the highest is under the beam.

Moreover, far from the center of the laser beam, between 11 μ m and 14 μ m, the emission temperature, the electron and the hole temperatures can be considered to be equal to the lattice temperature, because they are around 288K, and that the difference observed on the figure could be attributed to the uncertainty of the performed fit, estimated to be about 5K. Last, the hole have a temperature that increases later than that of the electrons.

Figure 2 (b) shows the variation of the electrochemical potentials with the distance. First, we observe that the electrochemical potential of the electrons is higher than that of the holes by 80 meV. Second, the electrochemical potential of the carrier is not symmetric and that of the electrons (in circles) increases while approaching the center of the laser beam, in a same trend than the isothermal electrochemical potential obtained with our developed isothermal full spectrum fit method, displayed in triangles. Last the electrochemical



(a) Temperature



(b) Electrochemical potentials: $\triangle = \mu_\gamma$, $\circ = \mu_H^e$, $\square = \mu_H^h$

Fig. 2. Variation of the temperatures and electrochemical potentials with the distance from the center of the laser beam, on the hyperspectral photoluminescence data recorded at the lowest incident photon flux.

potential of the holes increases and remains constant.

IV. CONCLUSION

Starting from the classical generalized Planck's law we have developed a non-equilibrium generalized model to describe hot carrier photoluminescence spectra. However this approach was not successful until we wrote a new non-equilibrium generalized Planck's law taking into account the variation of the absorptivity with the temperature and electrochemical potentials of the carriers. This last expression has been successfully used to fit absolutely calibrated hot carrier photoluminescence spectra to obtain different electron and hole temperatures as well as different absolute electrochemical potentials for each type of carrier. Last we use these results to compute different electron and hole thermalization coefficients.

This work shows an increased accuracy in the fit of hot carrier photoluminescence spectra. The theoretical approach and the experimental results can be useful to have a better insight into the separate hot carrier thermodynamical properties of electrons and of holes. These thermodynamical carrier properties give new opportunities for both photovoltaic and thermoelectric effects: indeed this approach is a first step before characterizing transport properties such as thermopower [15], thermal and electrical conductivity of a sample, with *one contactless* hot carrier photoluminescence measurement.

ACKNOWLEDGMENT

The authors are grateful to the French ministry of Ecology, Sustainable Development and Energy for the PhD grant of François Gibelli and to NextPV and the French embassy in Japan for a visit of François Gibelli there, where some of the work could be carried out. Part of this work was performed in the framework of the program "New concepts in photovoltaics" at IPVF under contract ANR-IPVF-02.

REFERENCES

- [1] P. Würfel, "The chemical potential of radiation," *Journal of Physics C: Solid State Physics*, vol. 15, no. 18, p. 3967, 1982. [Online]. Available: <http://iopscience.iop.org/0022-3719/15/18/012>
- [2] J. Rodière, L. Lombez, A. Le Corre, O. Durand, and J.-F. Guillemoles, "Experimental evidence of hot carriers solar cell operation in multi-quantum wells heterostructures," *Applied Physics Letters*, vol. 106, no. 18, p. 183901, May 2015. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/106/18/10.1063/1.4919901>
- [3] A. Delamarre, "Characterization of solar cells using electroluminescence and photoluminescence hyperspectral images," *Journal of Photonics for Energy*, vol. 2, no. 1, p. 027004, Jul. 2012. [Online]. Available: <http://photonicsforenergy.spiedigitallibrary.org/article.aspx?doi=10.1117/1.JPE.2.027004>
- [4] L. C. Hirst, R. J. Walters, M. F. Fhrer, and N. J. Ekins-Daukes, "Experimental demonstration of hot-carrier photo-current in an InGaAs quantum well solar cell," *Applied Physics Letters*, vol. 104, no. 23, p. 231115, Jun. 2014. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/104/23/10.1063/1.4883648>
- [5] M. Planck, *Vorlesungen ber die Theorie der Warmestrahlung*. Leipzig: Verlag von Johann-Ambrosius Barth, 1906.
- [6] R. T. Ross, "Efficiency of hot-carrier solar energy converters," *Journal of Applied Physics*, vol. 53, no. 5, p. 3813, 1982. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/53/5/10.1063/1.331124>
- [7] F. Gibelli, L. Lombez, and J.-F. Guillemoles, "Quasi-equilibrium Generalized Planck's law from Fermi-Dirac distributions of both electrons and holes," *Physica B - In revision*.
- [8] B. R. Bennett, R. A. Soref, J. del Alamo, and others, "Carrier-induced change in refractive index of InP, GaAs and InGaAsP," *Quantum Electronics, IEEE Journal of*, vol. 26, no. 1, pp. 113–122, 1990. [Online]. Available: http://ieeexplore.ieee.org/xpls/abs_all.jsp?arnumber=44924
- [9] R. J. Elliott, "Intensity of Optical Absorption by Excitons," *Physical Review*, vol. 108, no. 6, pp. 1384–1389, Dec. 1957. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRev.108.1384>
- [10] C. G. Kuper and G. D. Whitfield, *Polarons and excitons*, 1st ed. New York: Plenum Press, 1963.
- [11] M. Shinada and S. Sugano, "Interband Optical Transitions in Extremely Anisotropic Semiconductors. I. Bound and Unbound Exciton Absorption," *Journal of the Physical Society of Japan*, vol. 21, no. 10, pp. 1936–1946, Oct. 1966. [Online]. Available: <http://journals.jps.jp/doi/abs/10.1143/JPSJ.21.1936>
- [12] Chemla, "Room Temperature Excitonic Nonlinear Absorption and Refraction in GaAs/AlGaAs Multiple Quantum Well Structures," *IEEE journal of quantum electronics*, vol. QE-20, no. 3, pp. 265–276, 1984.
- [13] Y. Chen, R. Cingolani, L. C. Andreani, F. Bassani, and J. Massies, "Photoluminescence in quantum well and bulk GaAs: a direct comparative study," *Il Nuovo Cimento D*, vol. 10, no. 7, pp. 847–859, 1988. [Online]. Available: <http://link.springer.com/article/10.1007/BF02450144>
- [14] A. Delamarre, L. Lombez, and J.-F. Guillemoles, "Contactless mapping of saturation currents of solar cells by photoluminescence," *Applied Physics Letters*, vol. 100, no. 13, p. 131108, 2012. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/100/13/10.1063/1.3697704>
- [15] F. Gibelli, L. Lombez, J. Rodière, and J.-F. Guillemoles, "Optical Imaging of Light-Induced Thermopower in Semiconductors," *Physical Review Applied*, vol. 5, no. 2, Feb. 2016. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevApplied.5.024005>