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In a Comment on a previously published article in this Journal [Phys. Rev. Applied 5, 024005 (2016)][1], Apertet states that *the definition of the thermopower given in that article seems erroneous due to a confusion between the different physical quantities needed to derive this parameter.* We believe some definitions need to be clarified in order to avoid confusions. We here intend to answer the questions of Apertet by detailing the method and by focusing on the definition of the quantities we optically measured.

INTRODUCTION

The original paper draws from both photovoltaics and thermoelectrics in order to have a better insight into the working principle of hot carrier solar cells, with the risk that, in doing so, some traditional wisdom of each field may become inoperative. Hot carrier solar cells is a very promising concept to achieve high photon conversion yields, by converting the excess of kinetic energy of the carriers into potential electrical energy faster than the carrier energy is transferred to the lattice of the material (thermalization). In these devices, the photogenerated carriers, electrons and holes, are in electrochemical quasi equilibrium for carriers of the same sort, and in electrochemical non-equilibrium for carriers of opposite sort (as there are in classical photovoltaics) and also in thermal non-equilibrium with the lattice. Because the device converts electrochemical energy between different temperatures, thermoelectric effects become important and have to be dealt with, contrary to classical photovoltaics where such effects can be neglected. This is the context of our study, and it differs from the usual context of thermoelectricity, where only one type of carrier has to be taken into account.

The other peculiar point of our study is that we have used purely optical methods to investigate electrochemical energy conversion in solar cells, including hot carrier solar cells.

The experiment presented in the original research article uses the generation of hot carriers in an intrinsic quantum well structure of InGaAsP with a laser beam. The data are obtained with the analysis of photoluminescence spectra that are spatially and spectrally resolved.

The experiment evidenced gradients in carrier temperatures and electrochemical potentials, with the consequence that thermoelectric effects should be involved. As pointed out in the original article and in the comment, the thermoelectric effect is measured in conditions differing from those used classically for Seebeck coefficient measurement (single carrier type, open circuit measurement): the property measured here is ambipolar and does not follow from local equilibrium of carriers with lattice. These points were insufficiently developed in our original paper.

Here we take advantage of the comment from Apertet to develop the method and encourage other scientists to improve the initial work. Indeed we discuss the validity of the method and we explain the definition of the quantities involved in the optical measurement of the thermopower. This will constitute the main part of this paper, while we will also answer at the end of the text the other questions raised that resulted from obvious misunderstanding of the original paper.

I. ON THE VALIDITY OF THE EXPERIMENTAL METHOD

On appearance, our optical measurements look similar to traditional Seebeck coefficient measurements. First, as stated in the introduction of the Comment, the classical measurement of a Seebeck coefficient is made in open circuit conditions, that are fulfilled in the original experiment: there is no electrical contact between the sample and an external electrical circuit. Second, a linear dependence is found between the measured temperature gradient and a linear combination of electrochemical potentials of the carriers (their difference, actually, i.e. the quasi Fermi level splitting), as shown in figure 3a of the original research article. But, on the one hand, the sample is intrinsic and net carrier currents are present in the sample during the measurement, and on the other hand, the ration of the quasi Fermi level splitting gradient to the temperature gradient needs to be more rigourously related to the Seebeck coefficient of the electrons and holes.

1. Preliminary considerations

The local laser excitation induces a lateral current due to the carrier diffusion[2]. The optical method we originally presented relies on the facts that (a) the local heat

transport and carrier transport are unequivocally related at the local scale, (b) that carrier transport can be extracted from the measured quasi Fermi level (QFL) splitting. These points deserve some attention as in ambipolar diffusion, the total number of carriers is not necessarily conserved (electron and holes can recombine, e.g. radiatively), so that the QFL splitting gradient has a contribution not only from changes in carrier temperature but also changes in carrier population. In other words the heat dissipation (carrier cooling) should be large as compared to the recombination processes (carrier losses), so that the carrier cooling could be assumed to occur at constant carrier population.

This assumption is reasonable because, indeed, carrier intra-band thermalization is a much faster process (ps) than inter-band population relaxation times (ns) in the system considered. This is further supported by figure 2 of the original paper where it is apparent that the temperature gradient relaxes over a dozen of microns, while, at constant temperature, the carrier do not relax appreciably (quasi constant QFL splitting) over the image (100's of microns).

2. *Relation of transport coefficient in the original paper to conventional transport coefficients*

We start by using the Onsager's relations taken from a fluid model[3]. The equation system defines the current and heat fluxes. If one focus on the current flux, each current density (electrons and holes) is given by:

$$\overrightarrow{J_N^e} = - L_{qq}^e \overrightarrow{grad}(\eta^e) - L_{qs}^e \overrightarrow{grad}(T^{w,e}) \quad (1)$$

$$\overrightarrow{J_N^h} = - L_{qq}^h \overrightarrow{grad}(\eta^h) - L_{qs}^h \overrightarrow{grad}(T^{w,h}) \quad (2)$$

$$\text{where : } L_{qq}^{e,h} = \frac{\sigma^{e,h}}{e^2} \quad (3)$$

$$L_{qs}^{e,h} = \frac{\alpha_H^{e,h}\sigma^{e,h}}{e} \quad (4)$$

$$\eta^e = \mu^e + k_b T^{w,e} \ln(\frac{n}{N_C}) - |e|V \quad (5)$$

$$\eta^h = \mu^h + k_b T^{w,h} \ln(\frac{p}{N_V}) + |e|V \quad (6)$$

where L_{qq} and L_{qs} are matrix parameters related to macroscopic material parameters: $\sigma^{e,h}$, $\alpha_H^{e,h}$, $\eta^{e,h}$, $\mu^{e,h}$, which are respectively the conductivity, the Seebeck coefficient, the electrochemical potential, and the chemical potential of electrons and holes. As usual, Nc and Nv are the effective density of states of, resp., the conduction and the valence bands. V is the local electrostatic potential, n and p are ,resp., the local electron and hole concentrations. As the temperature measured is a temperature of the electron-hole pair T^w, one can consider $T^w = T^{w,e} = T^{w,h}$. Moreover, as the quantum well region is undoped and the optical excitation generates as many electrons as holes, the diffusion of both carriers have to be taken into account.

The carriers are not extracted in an external circuit, therefore, after their diffusion, photogenerated carriers will have to recombine among themselves, meaning $\overrightarrow{J_N^e} + \overrightarrow{J_N^h} = 0$. Thus, addition of Eq. (1) and Eq. (2) gives:

$$L_{qq}^e \overrightarrow{grad}(\eta^e) + L_{qq}^h \overrightarrow{grad}(\eta^h) + (L_{qs}^e + L_{qs}^h)\overrightarrow{grad}(T^w) = 0 \quad (7)$$

Let us remind:

$$\eta^e = E_{fn}$$
$$\eta^h = -E_{fp}$$
$$\mu_\gamma = \eta^e + \eta^h$$

where E_{fn} and E_{fp} are the quasi-Fermi levels electrons and holes. As we *optically* measure their difference (μ_γ), one must write out an average matrix term $\bar{L}_{qq}$ and its matching term $\tilde{L}_{qq}$:

$$\bar{L}_{qq} = \frac{L_{qq}^e + L_{qq}^h}{2} \quad (8)$$

$$\tilde{L}_{qq} = \frac{L_{qq}^e - L_{qq}^h}{2} \quad (9)$$

so μ_γ appears in Eq. (7) as:

$$\begin{aligned} \bar{L}_{qq}\overrightarrow{grad}(\mu_\gamma) + (L_{qs}^e + L_{qs}^h)\overrightarrow{grad}(T^w) \\ + \tilde{L}_{qq}\left[\overrightarrow{grad}(\eta^e) - \overrightarrow{grad}(\eta^h)\right] = 0 \end{aligned} \quad (10)$$

If one details the right term $\left[\overrightarrow{grad}(\eta^e) - \overrightarrow{grad}(\eta^h)\right]$ according to Eq. (5) and Eq. (6) knowing that there is no change in the material composition along the lateral direction $\overrightarrow{grad}(\mu_0^{e,h}) = 0$ and no electric field is $\pm qV = 0$, one gets:

$$\begin{aligned} \left[\overrightarrow{grad}(\eta^e) - \overrightarrow{grad}(\eta^h)\right] = \\ \overrightarrow{grad}\left[k_b T^{w,e} \ln\left(\frac{n}{N_C}\right)\right] - \overrightarrow{grad}\left[k_b T^{w,h}\left(\frac{p}{N_V}\right)\right] \end{aligned} \quad (11)$$

As we assume $T^{w,e} = T^{w,h} = T^w$ and $n \approx p$, thus the equation becomes:

$$\begin{aligned} \left[\overrightarrow{grad}(\eta^e) - \overrightarrow{grad}(\eta^h)\right] = \\ \overrightarrow{grad}\left[k_b T^w \ln\left(\frac{N_V}{N_C}\right)\right] \end{aligned} \quad (12)$$

temperature becomes the only term, which depends on the direction.

In a direct band gap semi-conductor quantum well $\frac{N_V}{N_C} = (\frac{m_h}{m_\Gamma})$, where m_h is the effective hole mass and m_Γ is the electron mass in the center of the Brillouin zone (Γ), thus:

$$\begin{aligned} \left[\overrightarrow{grad}(\eta^e) - \overrightarrow{grad}(\eta^h)\right] = k_b \ln(\frac{m_h}{m_\Gamma})\overrightarrow{grad}(T^w) \\ = C \times \overrightarrow{grad}(T^w) \end{aligned} \quad (13)$$

Thereby equation Eq. (10) writes:

$$-\frac{\overrightarrow{grad}(\mu_\gamma)}{\overrightarrow{grad}(T^w)} = \frac{L^e_{qs} + L^h_{qs} + \tilde{L}_{qq} \times C}{\bar{L}_{qq}} \tag{14}$$

At last, if one replaces $\bar{L}_{qq}$ and $\tilde{L}_{qq}$, which write as Eq. (8) and Eq. (9) by Eq. (3) and Eq. (4), in Eq. (14):

$$-\frac{\overrightarrow{grad}(\mu_\gamma)}{\overrightarrow{grad}(T^w)} = 2e\frac{\alpha^e_H\sigma^e + \alpha^h_H\sigma^h}{\sigma^e + \sigma^h} + \frac{\sigma^e - \sigma^h}{\sigma^e + \sigma^h} \times C \tag{15}$$

In the equation, one can recognize an intrinsic Seebeck coefficient α^i_H, which writes as:

$$\begin{aligned} \alpha^i_H =& \frac{\alpha^e_H\sigma^e + \alpha^h_H\sigma^h}{\sigma^e + \sigma^h} \\ \text{where : } \sigma^e =& -en\bar{\mu}^e \\ \sigma^h =& en\bar{\mu}^h \end{aligned} \tag{16}$$

Here, $\bar{\mu}^{e,h}$ are the electron and hole mobilities, therefore Eq. (14) becomes:

$$\begin{aligned} \alpha^i_H &= \bar{\alpha}^i_H - \frac{1}{2e}\frac{\overrightarrow{grad}(\mu_\gamma)}{\overrightarrow{grad}(T^w)} \\ \text{where : } \bar{\alpha}^i_H &= \frac{k_b}{e}\left[\frac{1}{2}\ln\left(\frac{m_\Gamma}{m_h}\right)\right] \end{aligned} \tag{17}$$

The equation shows the Seebeck coefficient depends on a left hand-side term $\bar{\alpha}^i_H$, which only depends on the material itself (effective) and a right hand-side one, which is dependent on thermodynamic quantities gradients ratio. This result is analogous to Cai and Mahan's calculations, which evidence that the Seebeck coefficient α experimentally measured (phenomenological one) is the sum of an effective Seebeck coefficient $\bar{\alpha}$ (independent on the material doping) and the thermodynamic quantities gradients ratio in[4].

II. DEFINITION OF THE QUANTITIES INVOLVED IN THE SEEBECK COEFFICIENT

1. *In-plane electrochemical potential vs. edges of the sample*

The author of the Comment claims that the electrochemical potential difference is not adequate, since this quantity is related to the *edges of the sample*.

We first like to recall the exact quantity we experimentally assess. In fact, we measure a in-plane electrochemical potential difference. The electrochemical potential difference has been obtained by fitting the photoluminescence spectra with the generalized Planck's law. The photoluminescence spectra recorded are shown in figure 2b of the original article. On each spectrum, the peak is located at 0.78eV, which corresponds to the band gap energy of the InGaAsP quaternary alloy in the wells. So the local electrochemical potential difference (between electron and holes) obtained from this spectra is related to the open circuit voltage (i.e., the QLF splitting) inside the quantum wells, in a hot carrier regime and in the plane of the quantum wells.

2. *In-plane temperature variation*

The original research article focuses on the thermodynamic properties of the *carriers*. Since the photoluminescence data show only one peak related to the carriers in the wells, we measure an in-plane temperature variation of the carriers in the plane of the wells.

Second, it is important to clarify that the lattice of the material remains at ambient temperature during the whole experiment, due to the low thermalization rates of carriers in hot carrier absorbing materials that is a consequence of the low conversion rate of zone center polar optical phonons to acoustic ones.

The in-plane electrochemical potential difference and the in-plane temperature variation enable us to measure thermodynamical parameters in thermal and electrochemical non-equilibrium conditions, and that can be related to a photo-thermopower effect, as discussed in the previous section.

3. *Meaning of the measured thermopower*

Having checked out the theoretical consistency of the proposed approach, the quality of the experiment, as well as the data obtained through the analysis, the original article compares the coefficient that has been obtained with a value of a similar sample computed and published in the literature.

In the original article, the temperature and electrochemical potential differences relate to the carriers inside the Quantum Well material. The obtained thermopower coefficient is homogeneous with a Seebeck coefficient and is obtained with consistent data. It can be related to the transport coefficients of the individual carriers types, electrons and holes.

The Comment states that the original article promises that the new measurement technique will give the same value than the classical one. This is clearly not a fair statement: the original conclusion states that it will help research and give a value of the thermoelectric coefficient within the frame of this technique, and possibly extend the capability to investigate thermoelectricity at a finer scale.

The consistency of the experimental results with both the theory and experiments in thermoelectricity gives confidence to use this technique to gain a better understanding in material research even if there are differences between the classical measurement technique and that presented in the original paper. These differences, as they

are related to a different measurement settings, would actually help to have a better understanding of both thermoelectrics and hot carrier photovoltaics. The method presented is meant to complement, not substitute, classical Seebeck coefficient measurement techniques.

III. DATA CONSISTENCY

Apertet mentioned that the slope in figure 3a of the original article should be positive as the gradients of the electrochemical potential (in figure 2c) and the temperature (in Figure 2d) have both the same sign, so the slope should be positive. It is indeed the case but as we use the same expression as Apertet, we included the elementary charge (taken negative). This implicitly assumes that electrons contribute more to the thermoelectric effect, which we assumed because of the higher electron mobility in the system considered. This was not explicitly mentioned in the original paper and we thus take the opportunity to clarify that point.

Concerning figure 2 of the original article, it shows all the data that have been recorded. Apertet questions the fact that the electrochemical potential is not zero away from the center of the image where the optical excitation takes place. Indeed both carriers, electron and holes, diffuse away from the excitation spot and the luminescence (i.e. electrochemical potential) is not null.

Away from the central region, the carriers are fully thermalized (i.e. carriers are in thermal equilibrium with the lattice). Therefore the only power dissipation that arises is the carrier recombination, that occurs for instance via radiative emission. The optical method is valid when the heat power dissipation through thermalization is much larger than the dissipation through carrier recombination[5]. This might not be the case away for the center. Nevertheless, this region displays no temperature gradient, and is thus not appropriate for the study we propose.

CONCLUSION

The original article reported an innovative technique to measure thermoelectric effects in semiconductors, but did not discuss in detail the nature of the quantities measured. This lead to possible misunderstanding of the true findings exposed and some confusion as to what was really measured, as in the Comment by Apertet.

In this reply we have detailed the method by focusing on the definition of the Seebeck coefficient we optically measured. Especially we discussed the validity of the method, the definition of the out of equilibrium, ambipolar, Seebeck coefficient and the in plane character of the measurement.

[1] F. Gibelli, Jean Rodière, L. Lombez, and J.-F. Guillemoles. Optical imaging of light-induced thermopower in semiconductors. *Phys. Rev. Appl.*, 5(2) (2016).

[2] Jean Rodière, Laurent Lombez, Alain Le Corre, Olivier Durand, and Jean-François Guillemoles. Experimental evidence of hot carriers solar cell operation in multi-quantum wells heterostructures. *Appl. Phys. Lett.*, 106(18), 183901 (2015).

[3] Lars Onsager. Reciprocal Relations in Irreversible Processes. II. *Phys. Rev.*, 38(12), 2265–2279 (1931).

[4] Jianwei Cai and G. D. Mahan. Effective Seebeck coefficient for semiconductors. *Phys. Rev. B*, 74(7), 075201 (2006).

[5] Jean Rodière. *Optoelectronic characterization of hot carriers solar cells absorbers.* PhD thesis, UPMC, 2014.