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Experimental evidence of hot carriers solar cell operation in multi-quantum wells heterostructures

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We investigated a semiconductor heterostructure based on InGaAsP multi quantum wells (QWs) using optical characterizations and demonstrate its potential to work as a hot carrier cell absorber. By analyzing photoluminescence spectra, the quasi Fermi level splitting $\Delta\mu$ and the carrier temperature are quantitatively measured as a function of the excitation power. Moreover, both thermodynamics values are measured at the QWs and the barrier emission energy. High values of $\Delta\mu$ are found for both transition, and high carrier temperature values in the QWs. Remarkably, the quasi Fermi level splitting measured at the barrier energy exceeds the absorption threshold of the QWs. This indicates a working condition beyond the classical Shockley-Queisser limit. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919901>]

Photovoltaic (PV) devices suffer from two major losses (i) the non-absorption of the incoming light linked to the absorber band gap and (ii) the thermalization process linked to the electron-phonons interactions.^{1,2} Those set the Shockley-Queisser (SQ) limit of a single junction photovoltaic conversion efficiency and limit the possibility of a lower material usage and/or installation cost share by increasing cell efficiency. In most cells, thermalization is the larger of the two losses.

Hot-carrier solar cells (HCSCs)³ could reduce the thermalization losses by using materials, such as quantum wells (QWs) structures, where carrier thermalization is somewhat slower than in standard devices.⁴⁻¹⁶

Operation in a solar cell having constituents at several temperatures obeys a slightly different physics as compared to standard devices. Two supplementary effects need to be taken into account: heat flows between the various temperature reservoirs (quantified by the thermalization rates) and coupled particle and thermal flows (as in Seebeck and Peltier effects). We show below how these can manifest themselves in a two-temperature device.

The objective of the present paper is twofold: to study the physics of a bithermal solar cell and to demonstrate experimentally that a significant part of the loss of hot carrier kinetic energy through thermalization can be converted into an extra electrical potential, similarly to that appearing in thermal gradients (Seebeck effect).

To do so, we present photoluminescence (PL) study of multi quantum wells heterostructures to probe the potential of these structures in the scope of HCSCs, as these are well documented model samples for such investigations.⁴⁻¹⁵ The sample investigated here consists of five $\text{In}_{0.8}\text{Ga}_{0.2}\text{As}_{0.44}\text{P}_{0.56}/\text{In}_{0.78}\text{Ga}_{0.22}\text{As}_{0.81}\text{P}_{0.19}$ QWs embedded in doped InP claddings (see Fig. 1).

Several optical experiments have analyzed the carrier temperature increase with the excitation power, including by CW excitation at room temperature,^{17,18} but none has yet observed the effect on the Quasi Fermi Level splitting (QFLs). However, the QFLs is a key parameter as it can be seen as the electron-hole pair free energy. Moreover, under PL excitation and without electrical bias, it is a good measure of the open circuit voltage,^{2,19} falling within 10 meV of the Voc in a number of cases.²⁰⁻²² We have measured quantitatively the QFLs and the carrier temperature in both the QWs and the barrier energy region, using the methods developed in Refs. 18 and 23 and shortly outlined below.

The main results of this study are *primo* that in the QWs, carrier temperatures higher than 600 K can be reached for an absorbed power of 40 000 kW/m² (i.e., about 40 000 Suns, 1 Sun being 1000 W/m²). *Secundo*, measuring the QFLs in the device, we show that it can exceed the absorption threshold of the QWs. This is the experimental evidence that QWs structures can work as a hot carrier absorbers and go beyond the SQ limit. *Tertio*, we propose a physical description for such bithermal photovoltaic devices.

The PL measurement setup we used is a homemade confocal microscope, with controllable excitation and collection area. Photoluminescence spectra are recorded at different excitation powers ($\lambda_{\text{exc}} = 980$ nm) with a InGaAs based spectrometer and then analyzed using the generalized Planck's law^{19,24}

$$\Phi(\hbar\omega) = A(\hbar\omega) \frac{1}{4\pi^2 \hbar^3 c^2} (\hbar\omega)^2 \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu}{kT}\right) - 1}. \quad (1)$$

In Eq. (1), Φ is the luminescence emission, $\hbar\omega$ is the photon energy, A is the absorption, Ω is the solid angle of emission, \hbar is the reduced Planck's constant, and c is the speed of light.

Essentially, one may extract (i) the carrier temperature T when measuring the slope of the PL signal at high energy

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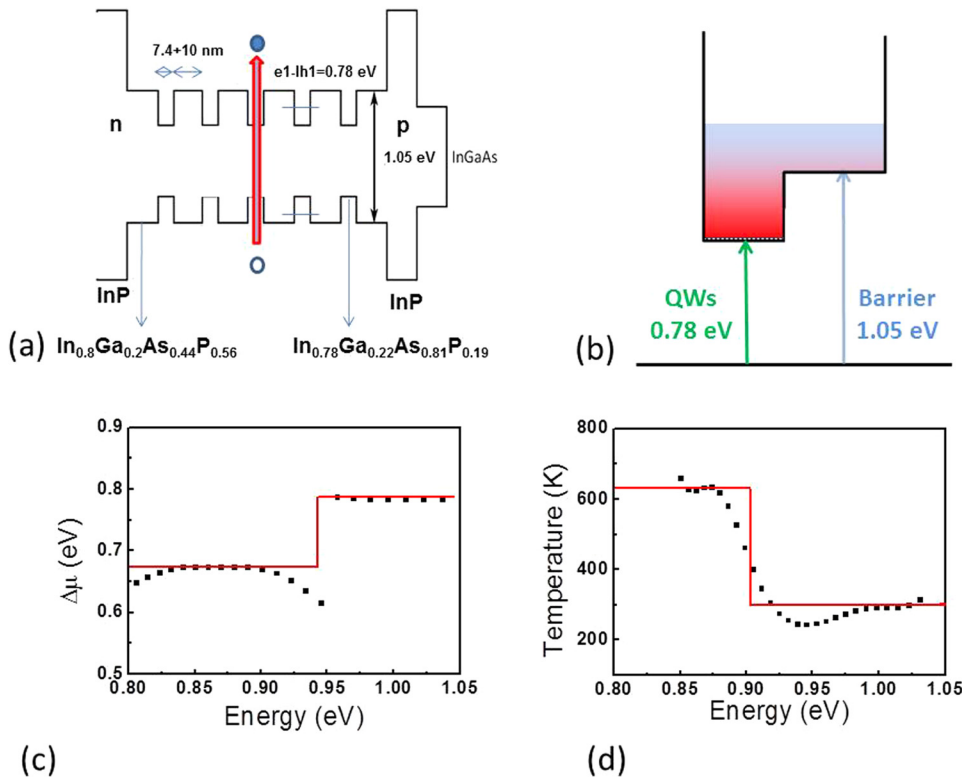


FIG. 1. (a) and (b) Illustration of the investigated Multi QWs sample. The carriers in the QWs display a high temperature. (c) and (d) Energy profile of the QFLs and the emission temperature, respectively. Black squares are experimental data and red lines are guide for the eyes.

and (ii) the QFLs $\Delta\mu$ from the absolute intensity of the PL signal and using the previously determined value of T .^{17,18,24–26}

Interestingly, it is possible to extract T and $\Delta\mu$ from Eq. (1) from different spectral ranges, i.e., corresponding to different transitions, therefore to either different electron populations or different materials or device regions.^{20–22,27}

The setup is calibrated by comparing data that have been recorded by a hyperspectral imager (HI) which has previously demonstrated its reliability on several PV absorber.^{21–23,26} The experimental results we present here are obtained with an equivalent collection and detection area, and the excitation power range varies from about 2000 kW/m^2 to $45\,000 \text{ kW/m}^2$ (this compared to 2000 and 45 000 Suns). It is worth noting that all the measurements are done at 300 K under CW excitation, which makes the measurements relevant for solar cell operation under concentrated solar flux.

As an example of the experimental data, we have represented the spectral variations $\Delta\mu(E)$ of the QFLs and $T(E)$ of the carrier temperature in Fig. 1 for an excitation power of about $30\,000 \text{ kW/m}^2$. The carrier temperature is much higher in the QWs energy range than in the barrier, whereas the $\Delta\mu$ is higher in the barrier. We will now discuss in more detail the variations of those two quantities.

Let us remind that the low energy part of the PL spectrum reflects the absorption properties and does not vary in the excitation power range we use; the temperature measured here is thus a carrier temperature (i.e., higher energy distribution), the lattice temperature remaining constant.^{18,24}

Carrier temperatures were studied as a function of the excitation power. Results are presented in Fig. 2 where green squares represent the carrier temperature within the QWs measured and the blue triangles indicate the carrier temperatures within the barrier energy region. In the excitation power

range we use, the latter temperature remains constant at ambient temperature. *A contrario*, temperatures as high as 600 K can be reached in the QWs region where the excitation power is equivalent to $46\,000 \text{ kW/m}^2$. Looking at the power dependence of the carrier temperature, we found a thermalization factor Q of about $4 \text{ W/m}^2/\text{K}$. According to numerical simulations,^{18,25} this value is sufficiently low to expect a potential conversion efficiency of more than 55%.^{18,25} Such high values had already been anticipated, based solely on carrier temperatures.^{17,18,28} To go beyond, it is necessary to evidence that the existence of high carrier temperatures can indeed be correlated into additional electrical work. Our approach was to measure the QFLs in this system as it represents the work generated per electron-hole pair (free energy).² It corresponds to the open circuit voltage as already shown.^{20–22}

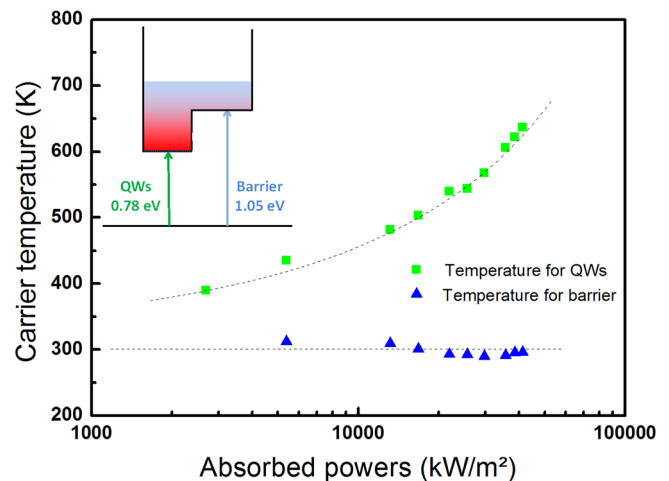


FIG. 2. Carrier temperatures in the quantum wells energy region (green squares) and in the barrier energy region (blue triangles). Inset: simple scheme of the situation of hot carriers in quantum wells vs cold in the barrier.

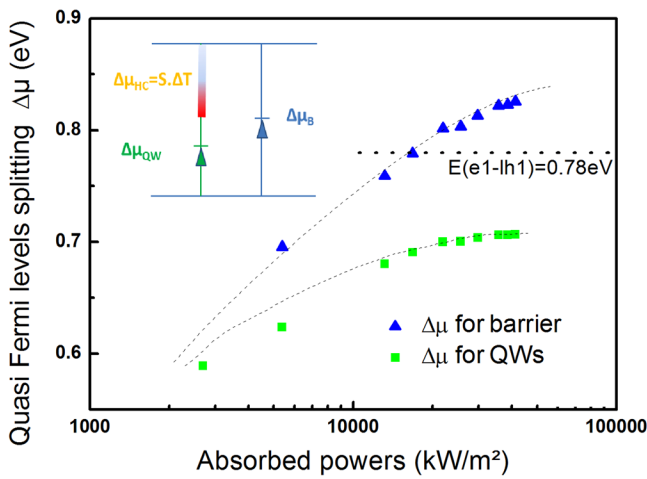


FIG. 3. Quasi Fermi level splitting in the quantum wells energy region (green squares) and in the barrier energy region (blue triangles). Dotted lines are guides for the eyes. Inset: Equivalent circuit of the hot carrier device with hot quantum wells (green diode) in parallel with cold barrier (blue diode) and equivalent Seebeck device (rectangle with color gradient).

The power dependence of the QFLs is presented in Fig. 3 with the same color code used in Fig. 2. From the quantum wells PL emission, the maximum $\Delta\mu$ observed reaches 0.70 ± 0.02 eV. This value has to be compared to the lowest transition value being the E1-LH1 transition at 0.78 eV. A difference of only 80 meV is found.

At low excitation power, the QFLs measured within the barrier energy region is close to the one measured in the QWs. This is a typical observation for classical QWs absorber (no hot carrier effect), no extra voltage being induced.^{27,29} At higher excitation power, a hot carrier population within the QWs is created and starts to be sufficient to induce an increase of the QFLs in the barrier. Remarkably, this effect is large enough that $\Delta\mu$ in the barrier exceeds the E1-LH1 transition. This fact evidences a decoupling of the maximum achievable voltage and the minimum energy absorption threshold. This is an essential indication that the sample can work as a hot carrier absorber with potential conversion efficiency beyond the Shockley Queisser limit.¹⁶

In fact, the sample could be represented by an equivalent electrical circuit represented in the inset of Figure 3. The barrier being a simple diode while the QWs are a diode connected in series with an equivalent thermoelectric device (pseudo-Seebeck effect) that converts the temperature gradient (extra kinetic energy) to an extra voltage. In classical system, with all carriers at room temperature, the QFLs in the barrier (i.e., its maximum achievable open circuit voltage at room temperature) will be limited by the QFLs of the QWs. Therefore, as the two systems are connected in parallel, the QFLs within the barrier will be limited to 0.78 eV. In HCSC absorber, this limitation does not take place, and the QFLs with the barrier could exceed 0.78 eV in that case. The data presented here are an experimental proof of such effect.

A last, very important point is that carrier extraction at the barrier level does not require a selective contact, since the carriers in this energy range are at room temperature. In other words, the barrier of the QWs can act as semi-selective contact (i.e., high energy pass filter).³⁰

The conversion of the hot carrier temperature found in the QWs into an extra electrochemical voltage can be seen as similar to a Seebeck effect, as it occurs in open circuit conditions. We introduce a pseudo Seebeck coefficient α' that can simply be calculated by the ratio:

$$\alpha' = \frac{\Delta\mu_b - \Delta\mu_w}{T_b - T_w}.$$

$\Delta\mu_b$ and $\Delta\mu_w$ are the QFLs in the barrier and in the QWs, respectively. T_b and T_w are the emission temperature in the barrier and in the QWs, respectively. We found an absolute value of $\alpha' = 350 \mu\text{V/K}$ at 40 000 Suns, which is in accordance with the Seebeck coefficient value reported in this type of material³¹ for electrons. The real meaning of this value, and its power dependence, will be discussed elsewhere. Yet, this result shows the potential to optically measure a Seebeck coefficient and shows the convergence between the HCSC concept and thermoelectricity.

In conclusion, both carrier temperature and absolute QFLs are measured in a HCSC potential absorber. Those values are measured for both the quantum wells and the barrier. Carrier population in the QWs exhibits high temperatures under concentration with a very low thermalization factor. This extra kinetic energy is efficiently converted into additional electrical work evidenced by the high QFLs measured in the barrier. Remarkably, QFLs in the barrier is larger than the E1-LH1 transition, providing an experimental demonstration that QWs structure could overcome the SQ limit when used as hot carrier absorber. We believe that this experimental evidence is not proper to the QWs sample investigated here and should be seen in equivalent structures that also exhibit a low thermalization factor.

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