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# Hot Carrier Photocurrent as an Intrinsic Loss in a Single Junction Solar Cell

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**Abstract.** In photovoltaics, hot carriers are mainly considered as a workforce for efficient hot carrier solar cells or as a reason of unfavorable heating of classical solar cells. Here we present experimental evidence of the hot carrier photocurrent, i.e., the current induced across a p-n junction by the hot carriers before their thermalisation. Competition between two photocurrents, the hot carrier and the generation-caused, is highlighted through excitation intensity, wavelength, sample temperature and bias voltage. The adverse impact of the hot carrier effect on the successful operation of a single junction solar cell is demonstrated, suggesting the need to discuss it as a novel form of intrinsic loss mechanism.

**Keywords:** solar cell, p-n junction, photocurrent, hot carriers
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## 1. Introduction

The rise of PCE (power conversion efficiency) of typical solar cells toward the Shockley-Queisser limit seems to be slowing down or even saturating [1]. Currently achieved 26.1% PCE for crystalline silicon solar cells is still well below the 31% limit predicted in 1961 [2]. The main stumbling blocks that hinder the minimization of this difference are categorized into extrinsic and intrinsic losses [3]. The first ones are theoretically avoidable. Two out of five intrinsic losses, namely, *the below $E_g$ loss* (non-absorption of photons with energy below the semiconductor bandgap) and *the thermalisation loss* are responsible for approximately 55% of the lost fraction of solar radiation at $E_g$ values corresponding to Si and GaAs [3]. The thermalisation loss deals with energy of the high-energy photons left after electron-hole pair generation which produces HCs (hot carriers) and which, on a picosecond timescale, is distributed to the lattice (Fig. 1a, process 3) [4]. The direct pre-thermalisational effect of HCs is neglected and their impact is accounted for only via the harmful heating of the lattice.

A number of concepts and cell designs, such as multijunction cells [6,7] or up- and down-conversion of photon energy, [8,9] have been proposed to minimize the intrinsic spectral losses and to approach the theoretical limits. Methods of hot carrier energy elimination [10] or harvesting before the thermalisation by means of impact ionization [11,12], nanostructures [13], or extraction through contacts [14-16] have been studied. The efficiency gain is achieved both by using the extra energy of HCs and by avoiding crystal lattice heating. Finally, an efficient solar cell operating purely on the basis of hot carrier phenomena has been proposed [17].

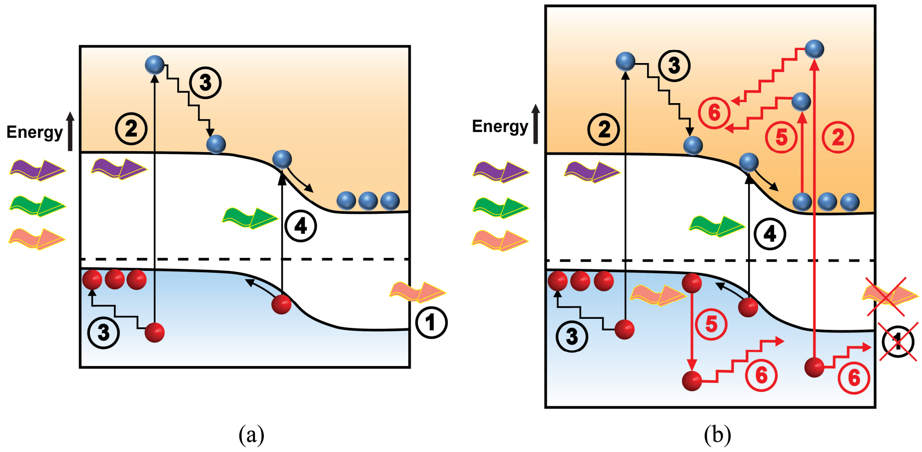



**Fig. 1.** a) Some aspects of a solar cell operation according to the classic model (adapted from) [5]: (1) non-absorption of below-bandgap photon, (2) absorption of above-bandgap photon, (3) thermalisation and diffusion of hot carrier in the bulk of the cell, (4) absorption of equal-to-bandgap photon and separation of generated electron-hole pair. b) Additional effects discussed in this work: (5) absorption of below-bandgap photons (intraband absorption, in contrast to process (1), (6) thermalisation of HCs and their simultaneous diffusion across the junction. Violet, green and orange arrows refer to corresponding ranges of incident light spectrum (high, medium and low energy photons, respectively).

Early research on hot carrier effects revealed that HC photoresponse is induced across a p-n junction by photons having energy much below the semiconductor bandgap (Fig. 1b, processes 5+6). In particular, $CO_2$ laser light (hν = 0.12 eV) induced HC photocurrent across Ge, Si and GaAs ($E_g$ = 0.66, 1.12 and 1.42 eV, respectively) p-n junctions [18-20]. Typical properties of the HC photocurrent were indicated as: *i*) its polarity showing no increase in carrier density (if carriers were generated from the intermediate bandgap levels, the photocurrent would have polarity the same as indicated by process 4 in Fig. 1); *ii*) fast temporal its behavior precisely following submicrosecond laser pulse since thermalisation of hot carriers occurs within the femtosecond to picosecond timescale, which is significantly shorter than the lifespan of the generated carriers). Spectral studies demonstrated HC photovoltage rise across the junction illuminated also by higher energy photons (Fig. 1b, processes 2+6) [21].

Thus, the role of hot carriers in the operation of a single p-n junction solar cell remains ambiguous. On the one hand, their direct impact is ignored by the classical theory of the PCE limit. On the other hand, HCs are evidenced and, despite their extremely short lifetime, are even harvested. The photoresponse of a p-n junction consists, on the whole, of three components caused by electron-hole pair generation, hot carriers, and lattice heating [22]. Here we give an account of the peak values of the first two of them simultaneously invoked by pulsed laser radiation, and show how they are the influenced by radiation intensity, wavelength and temperature. Current-voltage characteristics (I-Vs) with the two photocurrents having opposite directions are analyzed for the first time.

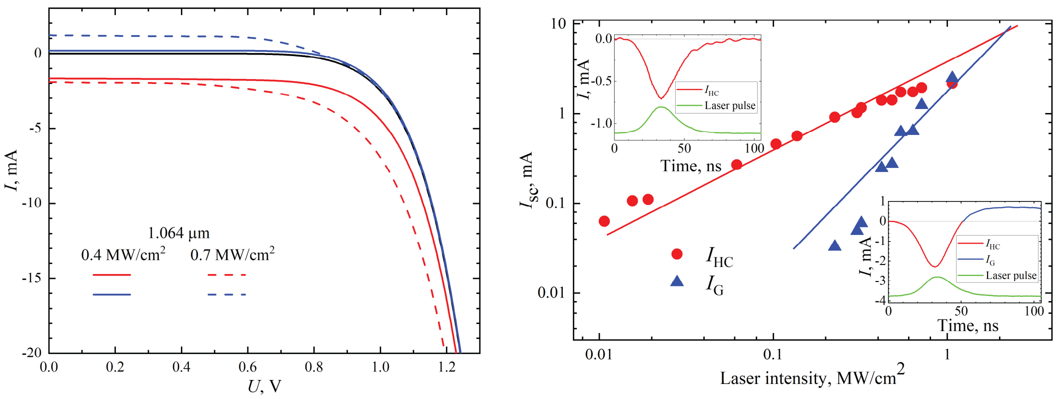
## 2. Experimental

GaAs and Si p-n junctions were chosen for the research; GaAs for its forbidden bandgap close to the theoretical value of the maximal possible efficiency of a single junction solar cell [3], and Si for its leadership in solar cell employment. GaAs samples were grown by liquid phase epitaxy (p-layer on n-substrate with respective carrier densities $5 \times 10^{17}$ cm$^{-3}$ and

$3 \times 10^{17}$ cm$^{-3}$) [21] with no antireflection coating, and narrow Au/Ge/Ni contacts were situated on the edge of the sample to avoid direct their exposure to laser radiation. Silicon diodes were cut from industrial solar cells (SoliTek, Vilnius, Lithuania). The samples were exposed to nanosecond-long laser pulses of 1.064 μm, 1.342 μm and 0.532 μm wavelength. High laser radiation intensity, higher than the natural sunlight, is a good tool to highlight the hot carrier effect.

## 3. Result and discussion

Low intensity (below 0.1 MW/cm$^2$), 17 ns-long laser pulse of 1.064 μm wavelength induces a photocurrent with polarity indicating carrier flow towards the barrier of the p-n junction (Fig. 1, stepped red arrows). Fast run, polarity and linear dependence on radiation intensity (see Fig. 2) are satisfactory arguments to attribute it to the HC current. As the excitation intensifies, a second photocurrent subpulse of opposite polarity appears (blue indications in Fig. 2 and elsewhere). The square dependence of its magnitude on the intensity stands for the two-photon absorption responsible for carrier generation. I-V characteristics in Fig. 2a show that the forward bias voltage is advantageous for the HC photocurrent in contrast to the generation-caused one. The rise of the laser intensity causes an increase of the hot carrier short circuit current $I_{SC\text{-}HC}$, and a much more expressed increase of the $I_{SC\text{-}G}$. This is the result of competition (note opposite polarities) of the two photocurrents and stronger (square) dependence of the generation component on the laser intensity.



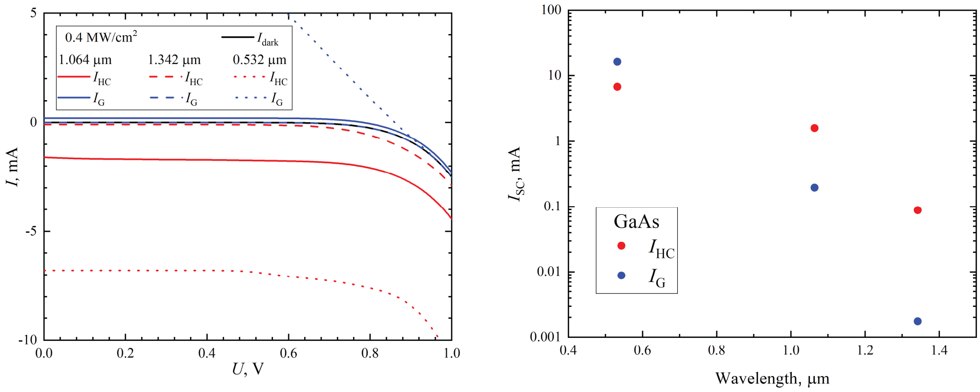

(a) (b)

**Fig. 2.** Power characteristics. a) I-Vs of GaAs p-n junction exposed to 1.064 μm laser radiation of 0.4 MW/cm$^2$ (solid lines) and 0.7 MW/cm$^2$ (dashed lines) intensity. b) Dependence of HC (red circles) and generation-induced (blue triangles) short-circuit photocurrent on laser intensity. Straight lines are guides for the eye of linear (red) and square (blue) dependence. Insets: typical photoresponse pulse under low (top-left) and high (bottom-right) laser intensities. Room temperature.

Fig. 3 shows spectral peculiarities of the two photocurrent components. When laser pulse of the same intensity but lower photon energy, i.e., 1.342 μm wavelength instead of 1.064 μm, is applied, the $I_G$ component naturally drops away. Another component $I_{HC}$ also decreases but to a smaller extent than $I_G$ does. Such a decrease is not representative of pure free carrier absorption which follows the classical $\propto \lambda^2$ law [23]. This means, that carrier heating, and correspondingly the HC photocurrent, are also related to carrier generation via the energy left over after the two-photon absorption: the change in photon energy from 1.17 to 0.93 eV results in decreased residual energy from 0.92 to 0.44 eV.

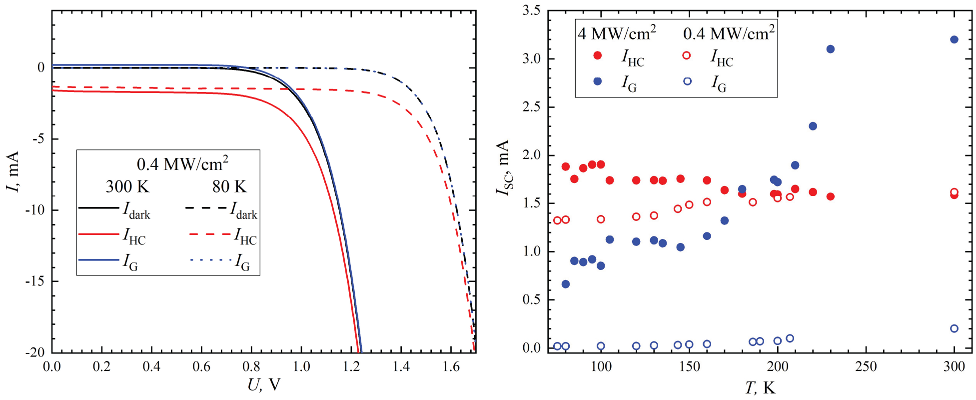
When higher energy photons are used (0.532 μm wavelength instead of 1.064 μm), the generation-related one takes the lead because of much stronger interband single-photon absorption. However, the residual 0.92 eV energy of the photon is supposed to be utilized for free carrier heating.

Usually, the hot carrier effects get pronounced at lower temperatures due to the increased carrier energy relaxation time [24]. The growth of HC photovoltage across n-n$^+$ and p-p$^+$ junctions under $CO_2$ laser light was observed with temperature change from 300 to 80 K [25]. When the GaAs p-n junctions are illuminated by 0.4 MW/cm$^2$ intensity 1.064 μm laser radiation, both photocurrent components, $I_{HC}$ and $I_G$, do not demonstrate strong dependence on temperature within the 300 – 80 K temperature range (Fig. 4). At higher radiation intensity (4 MW/cm$^2$) the generation current, which is relatively stronger at room temperature, drops sharply with the temperature, while the HC photocurrent even slightly increases (Fig. 4b, solid dots). Note that both the two-photon absorption coefficient and the free carrier absorption coefficient decrease with lower temperatures [26]. This again implies that the HC photocurrent does not depend only on the intraband absorption, but its magnitude results from the interplay or competition between the processes of carrier generation and carrier heating.



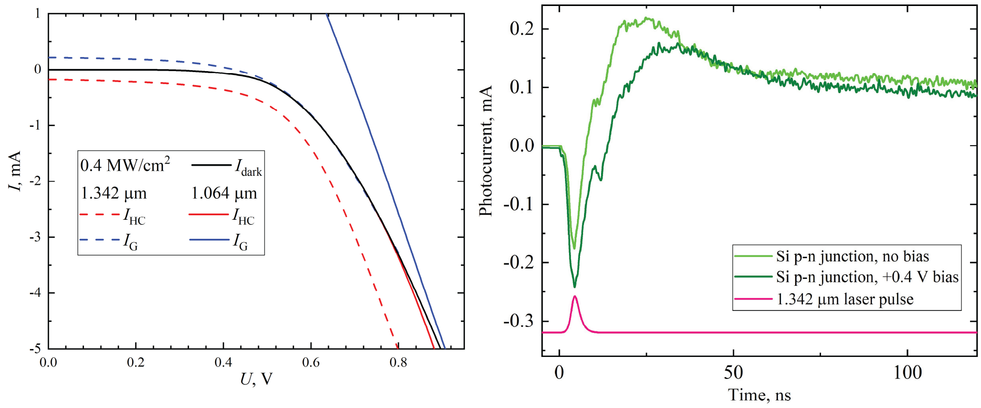

(a) (b)

**Fig. 3**. Spectral characteristics. a) I-Vs of GaAs p-n junction exposed to 0.4 MW/cm$^2$-intense laser radiation of 1.064 μm (solid lines), 1.342 μm (dashed lines) and 0.532 μm wavelength (dotted lines). b) Spectral dependence of short-circuit photocurrents caused by HCs (red dots) and carrier generation (blue dots). Room temperature.




(a) (b)

**Fig. 4.** Temperature characteristics. a) I-Vs of GaAs p-n junction exposed to 0.4 MW/cm$^2$-intense laser radiation of 1.064 μm at room (solid lines) and liquid nitrogen (dashed lines) temperatures. b) Dependence of short-circuit photocurrent $I_{SC\text{-}HC}$ (red dots) and $I_{SC\text{-}G}$ (blue dots) on temperature under 0.4 MW/cm$^2$ (open dots) and 4 MW/cm$^2$ (solid dots) laser radiation.




(a) (b)

**Fig. 5**. a) I-Vs of Si p-n junction exposed to 0.4 MW/cm²-intense laser radiation of 1.064 μm (solid lines) and 1.342 μm (dashed lines) wavelength. b) Typical shapes of photocurrent pulse under conditions of no (green) and forward +0.4 V (olive) bias voltage under the excitation of 1.342 μm wavelength laser pulse (below in pink). Room temperature.

In silicon p-n junction, the 1.064 μm radiation-induced hot carrier photocurrent is detected only at a sufficiently high forward bias (red solid line in Fig. 5a) when the potential barrier is low enough for the HCs to overcome and the impact of the generation photocurrent is weaker. Lower photon energy (wavelength 1.342 μm) makes lower $I_G$ and intensifies the HC component. Different reaction of the HC photocurrent to longer excitation wavelength in Si as compared to the GaAs case is most probably related to sharper spectral dependence of the interband absorption in this close-to-bandgap range and thus larger amount of energy left for direct free carrier heating via the intraband absorption.

## 4. Conclusions

To conclude, hot carrier photocurrent is present in a p-n junction independently of the excitation wavelength, intensity, and sample temperature, however, its input to the net photocurrent depends on these parameters and on semiconductor material and cannot be defined separately without considering its relation and competition with the carrier generation-caused photocurrent. Concerning the operation of a single-junction solar cell, four aspects are worth emphasizing in terms of the hot carrier phenomenon. *First*, before thermalisation, the hot carriers detrimentally condition the magnitude of the net photocurrent by forming photocurrent with polarity opposite to the classical generation-induced one. *Second*, the maximum power point of a solar cell occurs under certain conditions of forwardly biased junction what is beneficial to the flow of the HC photocurrent. *Third*, absorption of the below-bandgap solar spectrum should also be reckoned in when considering the PCE of a solar cell. *Fourth*, the hot carrier phenomenon could be included into the list of fundamental intrinsic losses of a solar cell.

**Conflicts of interest.** The authors declare no conflicts of interest.

## References

1. The National Renewable Energy Laboratory. (n.d.). Best Research-Cell Efficiency Chart. Nrel.Gov. Retrieved October 10, 2023. https://www.nrel.gov/pv/cell-efficiency.html.
2. Shockley, W., & Queisser, H. J. (1961). Detailed balance limit of efficiency of pn junction solar cells detailed balance limit of efficiency of pn junction solar cells*. *J. Appl. Phys. Addit. Inf. J. Appl. Phys. J. Homepage*, *32*.
3. Hirst, L. C., & Ekins-Daukes, N. J. (2011). Fundamental losses in solar cells. *Progress in Photovoltaics: Research and Applications*, *19*(3), 286-293.

4. Zhang, Y., Jia, X., Liu, S., Zhang, B., Lin, K., Zhang, J., & Conibeer, G. (2021). A review on thermalization mechanisms and prospect absorber materials for the hot carrier solar cells. *Solar Energy Materials and Solar Cells*, *225*, 111073.
5. Conibeer, G. (2007). Third-generation photovoltaics. *Materials Today*, *10*(11), 42-50.
6. De Vos, A. (1980). Detailed balance limit of the efficiency of tandem solar cells. *Journal of physics D: Applied Physics*, *13*(5), 839.
7. Kurtz, S., & Geisz, J. (2010). Multijunction solar cells for conversion of concentrated sunlight to electricity. *Optics express*, *18*(101), A73-A78.
8. Asahi, S., Teranishi, H., Kusaki, K., Kaizu, T., & Kita, T. (2017). Two-step photon up-conversion solar cells. *Nature Communications*, *8*(1), 14962.
9. Badescu, V., De Vos, A., Badescu, A. M., & Szymanska, A. (2007). Improved model for solar cells with down-conversion and down-shifting of high-energy photons. *Journal of Physics D: Applied Physics*, *40*(2), 341.
10. Saeed, S., De Jong, E. M. L. D., Dohnalova, K., & Gregorkiewicz, T. (2014). Efficient optical extraction of hot-carrier energy. *Nature Communications*, *5*(1), 4665.
11. Kolodinski, S., Werner, J. H., Wittchen, T., & Queisser, H. J. (1993). Quantum efficiencies exceeding unity due to impact ionization in silicon solar cells. *Applied Physics Letters*, *63*(17), 2405-2407.
12. Würfel, P. (1997). Solar energy conversion with hot electrons from impact ionisation. *Solar Energy Materials and Solar Cells*, *46*(1), 43-52.
13. Fast, J., Aeberhard, U., Bremner, S. P., & Linke, H. (2021). Hot-carrier optoelectronic devices based on semiconductor nanowires. *Applied Physics Reviews*, *8*(2).
14. Kempa, K., Naughton, M. J., Ren, Z. F., Herczynski, A., Kirkpatrick, T., Rybczynski, J., & Gao, Y. (2009). Hot electron effect in nanoscopically thin photovoltaic junctions. *Applied Physics Letters*, *95*(23).
15. Shayan, S., Matloub, S., & Rostami, A. (2021). Efficiency enhancement in a single bandgap silicon solar cell considering hot-carrier extraction using selective energy contacts. *Optics Express*, *29*(4), 5068-5080.
16. Esgandari, M., Barzinjy, A. A., Rostami, A., Rostami, G., & Dolatyari, M. (2022). Solar cells efficiency enhancement using multilevel selective energy contacts (SECs). *Optical and Quantum Electronics*, *54*, 1-9.
17. Ross, R. T., & Nozik, A. J. (1982). Efficiency of hot-carrier solar energy converters. *Journal of Applied Physics*, *53*(5), 3813-3818.
18. Umeno, M., Sugito, Y., Jimbo, T., Hattori, H., & Amemiya, Y. (1978). Hot photo-carrier and hot electron effects in pn junctions. *Solid-State Electronics*, *21*(1), 191-195.
19. Encinas-Sanz, F., & Guerra, J. M. (2003). Laser-induced hot carrier photovoltaic effects in semiconductor junctions. *Progress in Quantum Electronics*, *27*(4), 267-294.
20. Asmontas, S. P., Gradauskas, J., Seliuta, D., & Sirmulis, E. (2001, June). Photoelectrical properties of nonuniform semiconductor under infrared laser radiation. In *Nonresonant Laser-Matter Interaction (NLMI-10)* (Vol. 4423, pp. 18-27). SPIE.
21. Ašmontas, S., Gradauskas, J., Sužiedėlis, A., Šilėnas, A., Širmulis, E., Švedas, V., Vaicikauskas, V. & Žalys, O. (2018). Hot carrier impact on photovoltage formation in solar cells. *Applied Physics Letters*, *113*(7).
22. Gradauskas, J., Ašmontas, S., Sužiedėlis, A., Šilėnas, A., Vaičikauskas, V., Čerškus, A., Širmulis, E., Žalys 2 & Masalskyi, O. (2020). Influence of hot carrier and thermal components on photovoltage formation across the p–n junction. *Applied Sciences*, *10*(21), 7483.
23. Szuszkiewicz, W. (1996). IR absorption due to free carriers in GaAs. *EMIS DATAREVIEWS SERIES*, *16*, 235-243.
24. Dargys, A., & Kundrotas, J. (1994). Handbook on physical properties of Ge, Si, GaAs and InP. *Vilnius: Science and Encyclopedia Publishers, 1994.*
25. Asmontas, S. P., Gradauskas, J., Seliuta, D., Silenas, A., Sirmulis, E., & Marmur, I. Y. (1997, April). Photoelectrical properties of nonuniform GaAs structures under infrared laser illumination. In *Nonresonant Laser-Matter Interaction (NLMI-9)* (Vol. 3093, pp. 35-40). SPIE.
26. Krishnamurthy, S., Yu, Z. G., Gonzalez, L. P., & Guha, S. (2011). Temperature-and wavelength-dependent two-photon and free-carrier absorption in GaAs, InP, GaInAs, and InAsP. *Journal of Applied Physics*, *109*(3).

J. Gradauskas, O. Masalskyi, S. Ašmontas, A. Sužiedėlis, A. Rodin and I. Zharchenko. (2024). Hot Carrier Photocurrent as an Intrinsic Loss in a Single Junction Solar Cell. *Ukrainian Journal of Physical Optics*, *25*(1), 01106 – 01112.
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***Анотація.*** *У фотовольтаїці, гарячі носії головним чином розглядаються як робоча сила для ефективних сонячних батарей на основі ефекту гарячих носіїв або як причина* *небажаного нагріву класичних сонячних батарей. У цій роботі ми представляємо експериментальне підтвердження фотоструму гарячих носіїв, тобто струму, який індукований гарячими носіями через p-n перехід перед їх термалізацією. Конкуренція між двома фотострумами, струмом гарячих носіїв та генераційним струмом, висвітлюється через їх залежність від інтенсивності збудження, довжини хвилі, температури зразка та напруги. Демонструється негативний вплив ефекту гарячих носіїв на успішну роботу сонячної батареї з одним переходом, що вказує на необхідність обговорення його як нового виду внутрішніх втрат.*

***Ключові слова**: сонячний елемент, p-n перехід, фотострум, гарячі носії*