Fingerprints of non-thermal charge carrier distributions observed in the photocurrent of an InP photovoltaic structure at low temperatures.

Mathias Neges, Klaus Schwarzburg, Lars Gundlach, Lars Toeben, and Frank Willig
Hahn-Meitner-Institute, SE4
Glienicker Str. 100, 14109 Berlin, Germany,
email: schwarzburg@hmi.de

ABSTRACT

As a case study we have measured and modeled the probability of hot electrons in p-InP to reach a contact prior to undergoing thermalization. This information was deduced from characteristic LO-phonon emission dips in the excitation spectrum of the stationary photocurrent. The latter was measured at low light intensity over a wide temperature range (≥ 2K) in an energy window extending 0.3 eV above the conduction band edge. Monte Carlo simulations revealed firstly the loss mechanisms, secondly the characteristic parameter values for the scattering processes, and thirdly the probability of hot electrons to reach the contact prior to thermalization. For hot electrons higher up in the conduction band the principal trend towards shorter decay times combined with faster energy losses was established from real time femtosecond two-photon photoemission measurements in ultra-high-vacuum.

1. Introduction

So-called 3rd Generation Photovoltaic Devices aim at reducing the losses that arise from thermalization of hot carriers. In semiconductors the latter are generated via absorption of photons with energies well above the band gap. In some scenarios it is assumed that hot carriers can be collected at a contact or interface before suffering a significant loss in their energy [1]. The data presented here test this hypothesis with experimental data obtained on a real device. The measurements were performed for the InP/SnO2 contact at very low light intensities.

2. Experimental Results

Fig.1 shows the photocurrent excitation spectrum of the p-InP/n-SnO_2 heterojunction cell measured at 10K and 83K sample temperature. The sharp peak on the low energy side is attributed to excitons. The 10K curve shows a periodic modulation of the photocurrent. LO phonon scattering is here the dominant scattering process in InP. The positions of the dips in the spectrum (arrows) are controlled by scattering of conduction band electrons with LO phonon's (eq.1).

$$E = E_g + n\cdot\hbar\,\omega_0\left[1+\frac{m_e}{m_h}\right] \tag{1}$$

Here $\hbar\omega_0$=43.3meV [2] is the LO phonon energy and n is an integer. The linear fit extrapolates to the band gap energy of InP at 10K. From the gradient one obtains the value 0.099 for the ratio between the effective electron and hole masses, in good agreement with values in the literature provided m_h is assigned to the heavy hole [2]. Minima occur in the photocurrent spectrum at photon energies where the corresponding hot electrons can reach exactly the band edge by just emitting LO phonons.

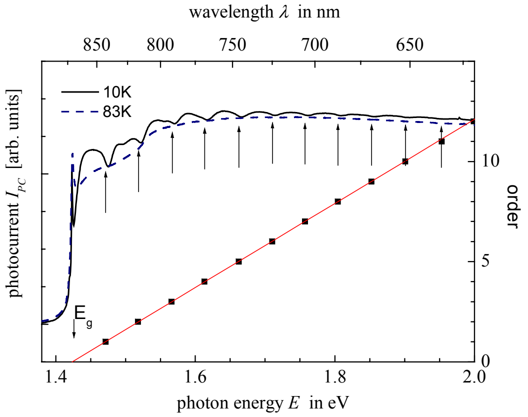

Fig.1 Photocurrent excitation spectra measured at 10K and 83K, respectively. The 83K curve is horizontally shifted to match E_g at 10K.

With increasing the temperature the maxima in between the LO phonon dips gradually disappear. The dashed curve in Fig.1 shows the spectrum measured at 83K. The photocurrent quantum yield is higher at low temperatures where the photon energy does not match the resonance described by eq.1. The dips are ascribed to two features. Firstly, LO phonon scattering is the dominant inelastic scattering mechanism at low temperatures (e.g. 10K). Secondly, the recombination probability is highest for electrons at the band edge. The dips correspond to the situation where electrons have the smallest probability for reaching the hetero interface and contributing to the photocurrent. At higher temperatures additional scattering processes become important and reduce the probability of the hot electrons to reach the band edge by just LO phonon scattering.

3. Monte Carlo Simulations

The goal of our simulations is understanding the scattering processes, the recombination events, and the temperature dependence seen in the measured photocurrent. The Boltzman transport equation (BTE) was solved by means of Monte Carlo techniques for electrons that were optically generated in the conduction band. The energy range relevant for our experiments (<0.4eV) allowed us to use a parabolic approximation for the conduction band. Scattering with LO-phonons, acoustic phonons, impurities, and holes was introduced into the model. Conduction band to acceptor recombination was used as the dominant recombination path. The charge separating hetero interface was mimicked as infinite sink for the electrons. The calculated distributions for the energy of the electrons that reach the contact are highly non-thermal. We verified that the simulations reproduced the key features seen in the excitation spectra of the photocurrents between 10K and 80K. This is the basis for extending the simulations and find out the energy distribution at 300K.

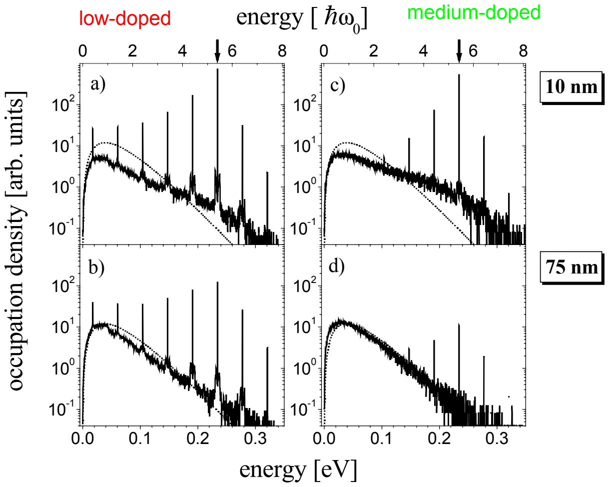

Fig.2 Energy distribution of electrons at T=300K that were generated at a distance of 10 and 75nm , respectively, from the interface acting as infinite sink. The electrons are generated 234meV above E_{CB}.

Fig.2 shows the energy distribution of photo-generated excess electrons at 300K for 2 different donor/acceptor concentrations. The Maxwell-Boltzmann distribution at 300K is shown as thin dashed curve for comparison. The distribution for electrons generated 10nm away from the interface is clearly non-thermal (Fig2.a,c). The spikes in the spectrum represent hot electrons contributing to the LO-phonon emission cascade. For higher dopant concentrations (c,d) as present in our cell, the cooling is faster due to a higher electron hole scattering rate. If the distance for generation of hot electrons is increased with respect to the infinite sink (Fig.2b,d), the electrons in the 'medium doped' simulation (Fig. 2d) are cooled down almost to the temperature of the lattice. There remains only a few percent difference between the Boltzmann distribution and the actual distribution.
To calculate the photocurrent one needs to sum over all the different contributions stemming from the different distances where the hot electrons are generated via photon absorption. The summation is weighted according to the absorption properties of InP. Fig.3 shows the energy flux of the electrons contributing to the photocurrent at the interface in the spectral range near the bandgap of InP. The energy flux of the 5800K Planck excitation source is shown for reference. The plot demonstrates that our real life material ('medium doped') has very little potential to be used efficiently in a hot electron converter since the deviation from a completely thermalized distribution is very small. Hot electrons can only be harvested from a layer extending a few tens of nanometers from the collector. In the investigated system electron hole scattering is the most effective cooling process at temperatures above 100 K. Thus, lower doping levels and a still better crystal quality could improve the chance for harvesting hot electrons at the contact (Fig.3 low doped curve).

For the proposed 3rd generation solar cells [1] the results presented here are the first step towards establishing a realistic model of hot electron behavior in a real material.

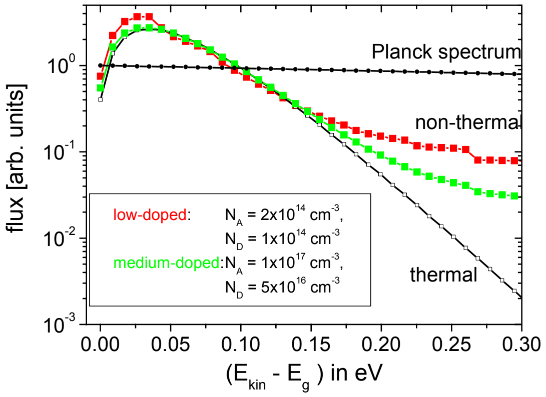

Fig.3 Calculated energy flux of the electrons contributing to the photocurrent at the interface at T=300K.

A large number of photons in the solar spectrum create hot electrons higher up in the conduction band than the 0.3 eV energy range probed in the above described experiments. Here the detailed band structure of the specific material has to be taken into account. The hot carrier decay is much faster than due to LO-phonon emission. In the case of III-V semiconductors there are processes like inter valley scattering with a small probability for the hot electron returning to the origin. The measured increase in the decay rate with increasing energy above the conduction band edge can be seen in Fig. 4. These data were measured with femtosecond two-photon photoemission (fs-2PPE) on MOCVD grown InP(100) that was transferred under ultra-high-vacuum conditions from the MOCVD reactor to the 2PPE chamber.. The decay rate depends on the occupancy of the final states for the scattering process [3].

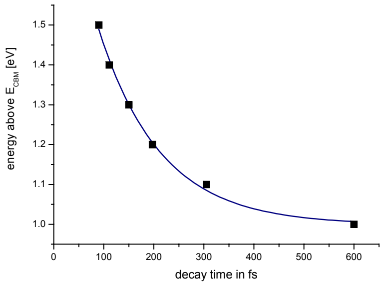

Fig.4. Increasing decay rate of hot electrons in InP for increasing energy above the conduction band edge

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