



Hot carrier solar cell with semi infinite energy filtering

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Abstract

Energy filtering of hot carriers in a solar cell may be attained by using band offsets at heterointerfaces. This rough energy filtering does not require special sophisticated energy filtering contacts, and may be implemented in the form of a double heterojunction. PbSe thin film as absorber layer was electrodeposited on InP single crystal. Experimental evidence of hot carrier filtering at InP/PbSe heterointerface at room temperature was obtained by double beam optoelectrical measurements. The measurements can be interpreted by thermionic emission over the band offset barriers. The valence band offset of 0.3 eV at the InP/PbSe heterointerface was measured by X-ray Photoelectron Spectroscopy. The filtering process may become useful for new generation of hot carrier solar cells.

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1. Introduction

The energy efficiency of conventional single junction solar cells is limited by not using photons with energy smaller than the band gap and by not using any excess photon energy larger than the band gap. This results in a modest maximal achievable efficiency of 31% without light concentration and 40.7% at full concentration, known as Shockley–Queisser limit (Shockley and Queisser, 1961; Luque and Marti, 2003). Several concepts were proposed to overcome this limitation; one of them is hot carrier solar cell (Ross and Nozik, 1982). This concept combines relatively simple design and high theoretical efficiency. Hot carriers are present in semiconductor shortly after absorption of a photon with energy larger than the band gap. This concept

describes, in fact, a heat engine based on expansion of hot electron gas, in a similar manner as a usual combustion engine utilizes the expansion of hot combustion gas. The efficiency limit of hot carrier concept is actually the Carnot efficiency, corrected for non-reciprocity of the optimal solar energy conversion process (Green, 2006). This limit is much higher than the Shockley–Queisser limit and amounts to 85% for full concentration. The traditional hot carrier cell concept utilizes a thin absorber layer and two contacts able to filter hot electrons and holes having their energies in a narrow energy range in the band away from the respective band edge (Fig. 1) (Würfel, 1997). Unfortunately, hot carrier solar cells were not successfully implemented so far, the reason being identified as too fast cooling of charge carriers in the bands of the absorber (Aliberti et al., 2010). The characteristic time of the cooling process is indeed very fast, in the picosecond range. In this paper, a concept is discussed, which is likely to help to overcome this difficulty.

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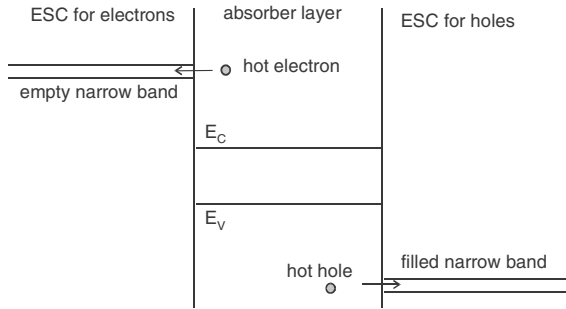


Fig. 1. Band diagram of a conventional hot carrier solar cell, simplified and adapted from Würfel (1997). ESC is energy selective contact, E_C conduction band edge, E_V valence band edge.

2. Concept description

The operation process of a hot carrier solar cell includes light absorption, transport of hot carriers towards the energy-selective contacts and collection of energy filtered hot carriers at solar cell contacts. The transport and the filtering steps together should be faster than the characteristic cooling time of charge carriers. Due to a high carrier temperature, the diffusion length of the hot carriers is surprisingly large. For example, for the cooling time of 10 ps, temperature 2500 K and carrier mobility of 2000 cm²/(V s), achievable in lead salts (Allgaier and Scanlon, 1958) and other narrow-gap materials, the diffusion length of hot carriers amounts to 650 nm. An absorber layer of about this thickness, made of a suitable narrow-gap direct semiconductor with large optical absorption coefficient, for example PbS, may be able to absorb most of the solar energy, if a decent light trapping scheme is used. The actual problem appears to be the energy filtering, because the narrow band energy selective contacts reflect most of the incoming hot charge carriers back into the absorber. This reflection allows much more time for carriers to cool down, than necessary for the carrier transport. The motivation for using narrow energy filtering is not only the desire to optimally utilize the energy of even hotter carriers, but also the concern, that carriers coming from the contact into the absorber layer may contribute to the cooling of the hot electron gas (Würfel, 1997). Using the analogy with a combustion engine, the optimal efficiency is achieved when the exhaust gas is at ambient temperature. However, this is not even nearly achieved in a usual combustion engine. No wonder, that major difficulties were encountered when implementing the perfect hot carrier solar cell. If hot carrier solar cell concept is to be successfully implemented at all, the requirements cannot remain that stringent.

The new concept considers energy selective contacts, which pass all charge carriers having energy larger than a certain minimal energy in the band (semi infinite filtering). The structure of the cell resembles a usual double heterojunction structure with large band offsets for the majority carriers (Fig. 2) and may be gradually derived starting from a conventional double heterojunction solar cell structure in a continuous technology development process by using

mixed crystal semiconductors. The theoretical limiting efficiency of more than 50% for the new concept was calculated elsewhere (Le Bris and Guillemoles, 2010). This paper is devoted to an attempt to implement experimentally and to test the new concept. We implemented a half of the structure of Fig. 2 using a combination of n-InP and PbSe.

3. Heterojunction formation

3.1. Substrate preparation

Nominally undoped *n*-type InP (111) wafers were obtained from NewWay Semiconductor Inc. with carrier concentration of nominally $0.8 \times 10^{16} \text{ cm}^{-3}$. The wafers were cleaved into $\sim 4 \text{ mm}^2$ chips and prepared as described below. 40 nm of gold were sputtered on the In-terminated side, then the Au film was tempered at 350 °C in vacuum ($2 \times 10^{-6} \text{ mBar}$) for 10 min. Contacts Au/n-In were characterized by force-sense three-electrode I–V measurement in the dark. Contact Au/n-InP shows ohmic characteristics with $\sim 50 \Omega \text{ mm}^2$ contact resistance. The substrates were mounted on copper-covered glass slides with silver conductive epoxy (CW2400, RS-components GmbH) and insulated by molding in epoxy resin. Substrates for X-ray Photoelectron Spectroscopy (XPS) measurements were used unmolded. The molded samples were then sequentially grinded with 60 μm and 15 μm SiC suspensions, polished with 1 μm , 0.1 μm diamond and 20 nm silica (Leco Co.). The plane termination by phosphorus of n-InP was confirmed by polishing etching test in 1 vol.% Br₂ in methanol. Prior to the electrochemical experiments the substrates were sequentially etched in 0.4 vol.% Br₂ in methanol, 3 M H₂SO₄ and rinsed with distilled water.

3.2. Electrochemical deposition of PbSe on InP

PbSe has been electrochemically deposited on n-InP(111)B according to the approach given in Froment

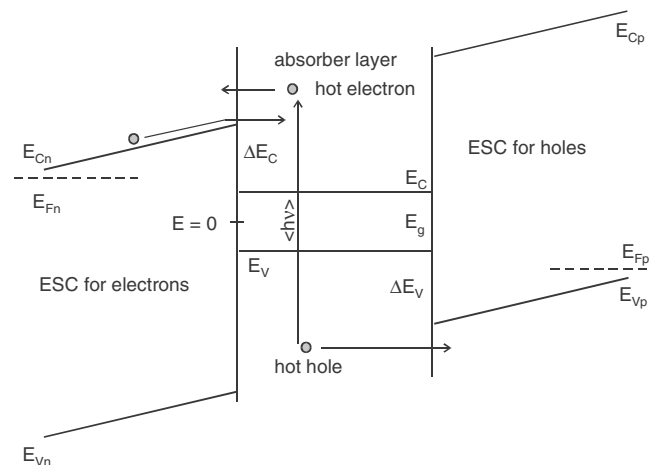


Fig. 2. Band diagram illustrating operation of hot carrier solar cell with semi infinite energy filtering.

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