Quasi Fermi Levels
in Semiconductor Photovoltaic Heterojunction

B.A. Orlowski, A. Pieniazek, K. Goscinski and K. Kopalko

Institute of Physics, Polish Academy of Sciences, al. Lotników 32/48, 02-668 Warsaw, Poland

The photovoltaic heterojunction elements are build of two different semiconductors of n and p type. Under cell illumination the same density of n and p carriers are created in each generation point but it leads to the remarkably higher increase of relative concentration for minority than for majority carriers. It is causing bigger energy change of the quasi Fermi level of minority than of majority carriers. The minority carriers decide of the value of generated photovoltage while the majority carriers contribution to it, in most cases can be neglected. Measured change of the generated open circuit photovoltage versus illumination light intensity allows to estimate corresponding to it increase of the minority carrier concentration. These allows as well to scan the part of the forbidden gap region by the minority carriers quasi Fermi level and in a case of impurity or defect levels located in forbidden gap it can influence on the continuous dependence of generated photovoltage versus light intensity e.g. for pinning of the Fermi level. To create efficient photovoltaic heterojunction it will need to study electronic properties of the used impurities and their proper distribution in the region of junction.

1. Introduction

The photovoltaic heterojunction elements can be built of semiconductor materials due to existence of two kinds of charge carriers, n-electrons and p-holes, in two separated conduction and valence bands, respectively. Heterojunctions are built of two semiconductors with different band gaps energies and each component contributes different minority and majority carriers. Recently, photovoltaic heterojunction properties are studied for two main purposes of application, like to construct efficient solar batteries [1–3] or as detectors of radiation [4]. For the case of solar batteries one of component of photovoltaic heterojunctions are p-type semiconductors with the moderate value of the energy band gap in the range of 1 to 2 eV, corresponding to the most effective materials to absorb radiation of the "sunny spectrum" (CdTe 1.5 eV, GaAs 1.45 eV, Si 1.2 eV). The second component in these photovoltaic heterojunctions are wide band gap n-type semiconductors, with the wide band gap energy in the range of 2 to 4 eV corresponding to the group of materials (GaN 3.4 eV, ZnO 3.37 eV, SiC 3.2 eV, ZnTe 2.25 eV) transparent in the energy radiation range highly absorbed by medium band gap semiconductors component partner (sunny spectrum). In this type of photovoltaic heterojunction the minority n-type carriers of medium band gap semiconductors component play the role of main creator of the electromotive force of the photovoltaic element.

The wide band gap n and p-type photovoltaic heterojunction of semiconductors of the energy band gap in the range from 2 to 4 eV are used to build ultraviolet radiation sensitive detectors [4].

2. Quasi Fermi levels and photovoltage of heterojunction

The electronic structure of the semiconductor photovoltaic heterojunction is presented in Fig. 1 as a junction of two different semiconductors with different band gaps and with different majority and minority electrons and holes. Contact of semiconductors in photovoltaic heterojunction leads to the creation of common thermal equilibrium Fermi level F for both sides 1 and 2 and it leads to the band bending and creation of electric field at the region of semiconductors contact of heterojunction. For n-type semiconductor (side 1) the equilibrium Fermi level is located at the top of the band gap close to the conduction band region. For p-type semiconductor (side 2) the F level is located at the low part of the band gap close to the valence band edge. The different band gaps and types of n or p carriers lead to the creation of electric field corresponding to the band bending at the junction region. In thermal equilibrium conditions minority carriers, electrons of part 2 in the region of heterojunction, are partially transported to the region of the opposite part side 1 of heterojunction due to the electric field. In thermal equilibrium conditions transported electrons create the diffusion current to compensate current caused by electric field. The similar effect occurs for the holes in semiconductor side 1. In the thermal equilibrium conditions, holes in semiconductor 1, in the region of heterojunction electric field E will be easily transported to the semiconductor 2 in the region of heterojunction. In thermal equilibrium conditions transported holes will create the opposite direction diffusion current to compensate hole current caused by electric field. The effects will be kept stable in the thermal equilibrium conditions and the current density will be equal to zero as the current created by electric field will be compensated by diffusion current.

The wide band gap of side 1 semiconductor (Fig. 1) allow to transmit the illumination light to the region of the junction and to generate electrons and holes effectively at the region of junction at the part of side 2.

For moderately intense continuous illumination of part 2 the thermal equilibrium conditions will be disturbed and they will be changed from the thermal

equilibrium to the steady state conditions. The electrons generated continuously in part 2 will cause the increase of the n concentration in conduction band of part 2 and the increase of number of electrons transported from part 2 to part 1. At the barrier it will lead to the increase of back diffusion current density of transported electrons and it will be compensated by increase of E field at the open circuit conditions.
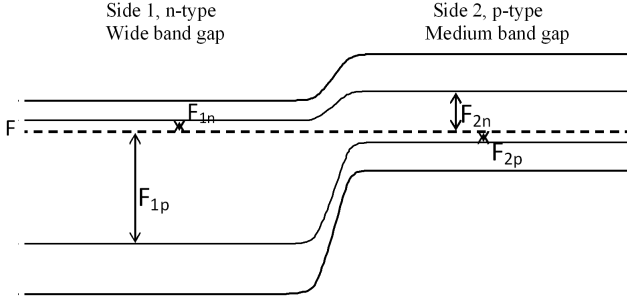

Fig. 1. Schematic electronic structure of heterojunction. F — Fermi level for thermal equilibrium, common for both sides of heterojunction. Side 1, s — type, wide band gap, F_{1p}, F_{1n} — changes of quasi Fermi levels of minority holes p and majority electrons n respectively after generation of $p = n$ carriers in side 1. Side 2, p-type, medium band gap, F_{2n}, F_{2p} — changes of quasi Fermi levels of minority electrons n and majority holes p respectively after generation of $p = n$ carriers in side 2.

Continuous generation of electrons in part 2 will lead to the increase of electrons concentration in the conduction band of part 2. This new value of the electrons concentration cannot be described by the same position of the thermal equilibrium Fermi level F. To describe the increase of concentration, only of electrons in part 2, the quasi Fermi level only for electrons in only of part 2 have to be introduced. This quasi Fermi level has to be shifted up on the energy F_{2n}, (see Fig. 1) over the Fermi level F. The quasi Fermi level F_{2n} represents the increase of the Fermi energy caused due to deviation from thermal equilibrium conditions to the steady state conditions (see Fig. 2).

In the analogical way like for electrons in part 2 the change of quasi Fermi level F_{1n} can be determined in part 1 (Fig. 1), under generation of electrons by proper illumination of part 1. The continuous generation of holes in part 2 leads to the increase of the p concentration at part 2. To describe this increase of concentration only for holes in part 2 the change of quasi Fermi level, only for holes and only in part 2, has to be introduced. This level has to be shifted down, on the energy F_{2p} (see Fig. 1) below the Fermi level F. This shifted Fermi level value will replace the Fermi level F in the Fermi–Dirac distribution function but only for holes in a case of the continuous steady state (see Fig. 2).

In the analogical way like for generated minority carriers electrons and holes in part 2 and 1 respectively, we can define two additional steady states quasi Fermi levels
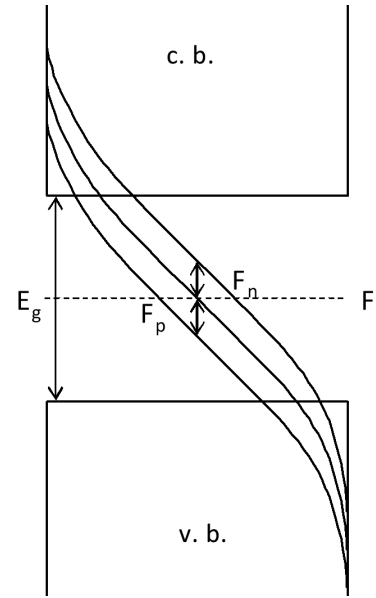

Fig. 2. Schematic comparison of the main bands electronic structure (v.b., c.b. and E_g) of semiconductor with the Fermi-Dirac function in thermal equilibrium (middle curve) and two curves corresponding to the steady state condition after steady illumination to generate of additional pairs of electrons and holes, shifted by correlated change of quasi Fermi levels above and below the middle curve for only electrons and only holes respectively. The upper curve describe the electrons distribution (above quasi Fermi level of electrons) and lower part describe the holes distribution (below quasi Fermi level of holes).

shifts F_{1n} and F_{1p} for majority carriers the electrons and holes in part 1 and 2 of heterojunction respectively (see Fig. 1) under continuous proper generation of $n = p$ in each particular point of the sample. As a consequence we will have four of steady state quasi Fermi levels shifts for free carriers: F_{1n}, F_{1p}, F_{2n}, and F_{2p}.

Electromotive force of open circuit voltage of illuminated heterojunction is built of the double contribution of two differences of quasi Fermi levels values of two opposite sides 1 and 2, of holes and electrons respectively. The difference of the value of quasi Fermi levels energies of electrons in the conduction band is

$$V_n = F_{2n} - F_{1n}$$

and the differences of holes quasi Fermi levels energies in the valence band is

$$V_p = F_{1p} - F_{2p}.$$

V_n, V_p are the open circuit voltage values correlated relatively to electrons in conduction bands and to the holes in valence bands carriers in steady state conditions.

The both open circuit voltages V_n and V_p contribute to the total open circuit voltage value V_{np}.

In the heterojunction the carriers of four bands interact, two conduction bands of different crystals and two of valence bands of different crystals. The interactions of electrons and holes in wide band gap materials are

weaker than it is in the medium band gap material. The conduction bands of both crystals are the creative partners of electrons dependent contribution of photovoltaic effect and the valence bands of both crystals contribute to create holes dependent photovoltaic contribution.

Values of F_{1n} and F_{2p} correspond to the shift of quasi Fermi Level of majority carriers electrons of side 1 and of holes of side 2 of heterojunction respectively. Under moderate illumination intensity, the relative changes of these majority carriers density are small in comparison to the corresponding changes of minority carriers F_{2n} and F_{1p} and can be treated as negligible small majority carriers contributions (F_{1n} and F_{2p}) to the V_n and V_p values. In this case only F_{2n} and F_{1p} values mainly contribute to the V_{np}.

Heterojunction is built of semiconductors with different band gaps and when the side 1 can be transparent ($h\nu \ll E_{g1}$ — band gap of side 1 component) for the illumination light, while the second semiconductor absorbs this light ($h\nu \geq E_{g2}$ — band gap of side 2 component) and minority n-type carriers of medium band gap semiconductors component will play the role of main creator of the electromotive force of the photovoltaic element.

If the generation of p and n carriers occurs only in the side 1, the total voltage will be reduced to the $V_{np} = F_{1p}$. In the case of generation p and n carriers only on the side 2 the total voltage will be reduced to the $V_{np} = F_{2n}$.

The particular interesting cases of the open circuit voltage value V_{np} can be measured directly for particular experimental conditions of e.g. partial illumination separately of side 1 or side 2 or both sides together. The interesting will be the contribution of high voltage generated in wide band gap semiconductor of part 1 and low voltage generated in semiconductor of part 2.

3. Summary and conclusions

Paper presents the application of quasi Fermi levels to describe the effect of generation of the open circuit voltage in photoheterojunction. The carriers of conduction and valence bands can create photovoltage like two independent cells. For some ranges of $h\nu$ energy illumination, when minority electrons are generated (side 2) the conduction bands cell will create the open circuit value. For illumination of other ranges of $h\nu$ energy, when minority holes are generated (side 1) the valence bands cell will create the open circuit value. For the case of common generation of minority electrons and holes the both cells will contribute to the open circuit voltage and allow to study of the influence on each other. The high band gap semiconductor side 1 can give higher contribution than lower band gap semiconductor side 2 to the open circuit voltage. These allows as well to scan the part of the forbidden gap region by the minority carriers quasi Fermi level and in a case of impurity or defect levels located in forbidden gap to determine the influence of it on the continuous dependence of generated versus light intensity e.g. for pinning of the Fermi level. Study of properties of used impurities and their proper contribution [5] will influence on properties of photovoltaic heterojunction.

References

[1] E. Przezdziecka, M. Stachowicz, S. Chusnutdinow, R. Jakela, A. Kozanecki, *Appl. Phys. Lett.* **106**, 062106 (2015).

[2] R. Pietruszka, G. Luka, K. Kopalko, E. Zielony, P. Bieganski, E. Placzek-Popko, M. Godlewski, *Mater. Sci. Semicond. Proc.* **25**, 190 (2014).

[3] S. Chusnutdinow, R. Pietruszka, W. Zaleszczyk, V.P. Makhniy, M. Wiater, V. Kolkovsky, T. Wojtowicz, G. Karczewski, *Acta Phys. Pol. A* **126**, 1072 (2014).

[4] M.A. Pietrzyk, E. Zielony, M. Stachowicz, A. Reszka, E. Placzek-Popko, A. Wierzbicka, E. Przezdziecka, A. Droba, A. Kozanecki, *J. Alloys Comp.* **587**, 724 (2014).

[5] L. Sosnowski, B. Orlowski, *Phys. Status Solidi A* **3**, 117 (1970).