Fermi Level Control and Thermal Current Densities in Selectively Doped P-I-N Multiquantum Well Photovoltaic Structures, Under Illumination

ARGYRIOS C. VARONIDES
Physics and Electrical Engineering Department
University of Scranton
800 Linden Street, Scranton PA, 18510
United States

Abstract: - III-V semiconductor multiquantum-well (mqw) photovoltaic devices show improved collection and transport properties when they are selectively doped. Existence of multiple quantum wells is of advantage because of (a) easier carrier collection (b) photocarrier separation (electrons vs holes) that reduces recombination and (c) of Fermi level shifting. The latter is of real advantage when the Fermi level is forced to be pinned within a quantum well, especially in the vicinity of the two sub-bands. Studying of the latter pinning is typically done via the neutrality equation. Charge neutrality condition is taken into account and includes (I) carriers contributed to quantum wells by shallow donor impurities embedded in the neighboring wide gap material (II) carriers contributed to the conduction band continuum (III) trapped carriers in the quantum wells, under dark conditions (IV) doping concentration levels and (V) layer widths. Under illumination, excess carriers are generated in the quantum wells, which thermally escape to the conduction continuum. Thermal currents are predicted to maximize at low temperatures, while significant current contribution is succeeded at high temperatures as well.

Key-Words: Fermi level, Quantum wells, photovoltaic heterostructures

1 Introduction

A common photovoltaic device design is to include a superlattice in the intrinsic region of a p/i/n heterostructure. The idea is to selectively dope the wide gap material of the multiquantum well structure, namely, AlGaAs (at 20-30% Al content) and keep the low gap material (GaAs) undoped so that the Fermi level will be forced to be shifted upwards in the quantum wells. Control of Fermi level E_F, may lead to novel devices with exceptional transport properties. This is because photocarrier energies depend directly on the negative exponential of the energy distance between Fermi level and conduction band E_C-E_F, so that as this energy is reduced due to Fermi level control, thermal escape of carriers is much easier to occur. A general relation for thermally escaping electrons is provided, and calculations indicate that appreciable thermionic current densities per quantum well are to be expected and of the order of 0.5-0.9mA/cm^2/individual quantum well,

before any scattering losses. Fermi level positions are predicted past the bottom of the quantum wells (GaAs layers at 5nm, 0.160eV qw depth, and at $6x10^{18}$ cm^{-3} doping), for instance, E_F is found to be only 50meV below the top of a quantum well, thus providing higher thermal currents when compared to bulk counterparts.

1 Neutrality Condition in the Window Layer

A multi-layered structure is assumed, consisting of N periods, each with a repeat distance $d=d_1+d_2$, where d_1, d_2 are the narrow and wide band gap materials respectively. Conduction carriers come from the contribution [1] of donor impurity centers, which already exist in the barrier regions of the selectively doped wide-gap layers, and from their conduction bands as well. Neutrality requires that the available concentration of electrons contributed by the donor impurities be equal to the carriers left behind at the donor levels, plus the carriers that remain in the quantum wells, plus the conduction band carrier concentration. The neutrality equation has been solved else where (with no illumination) and its solution expresses the energy difference between fermi level and conduction band edge of the lower band gap material. This expression includes parameters of both layers involved (GaAs-AlGaAs), namely, doping concentrations of the barrier material, widths of both layers, conduction band discontinuity and temperature.

For a 10-period multiquantum well structure, with 30% Aluminum content, activation energy values (E_C-E_F= ΔE_{CF}) range from 0.38eV to 0.32eV as doping levels increase from 10^{16} to 10^{18} cm^{-3} at 400 ^oK, and from 0.25eV to 0.18eV at room temperature and for the same doping variation. Activation energy values have been found to approach and pass the lowest conduction band at very low temperatures, namely, -0.05eV at 100^oK. At moderate doping levels (10^{17} cm^{-3}), activation energy values are of the order of 0.25eV at room temperature. Variation activation energy values has been found under different values of barrier material thickness. At room temperature, ΔE_{CF} is 0.1eV for a 10A potential width. Significant shift of the fermi level is predicted at low temperature (90^oK), where ΔE_{CF} is computed at –0.05eV (hence inside the quantum well), and for potential barrier width variation from 10 to 50A.

In summary, charge neutrality provides conditions for fermi level pinning at various temperatures and for a whole class of device parameters. At room and higher temperatures, under moderate doping levels the fermi level is pinned anywhere between 0.2 and 0.10 eV below the conduction band of the GaAs layer. Activation energy values may now be used in evaluating thermal currents out of these quantum wells, when the device is illuminated via photon flux at different wavelengths.

2 Thermionic currents in the Intrinsic Region

The device structure in mind is a p/i/n GaAs-AlGaAs solar cell [2,3,4] with the intrinsic region (length L_i) comprised of a sequence of quantum wells and potential barriers made out of low and wide gap GaAs and AlGaAs layers respectively. Miniband solutions are expected to exist in these finite quantum wells, so that they may serve as traps of photogenerated carriers arising from the

valence band after optical excitation. It is expected that illumination of the intrinsic region will cause direct generation of electron-hole pairs) thus contributing to increased carrier-concentration in each quantum well. Such population increase is expected to escape from the wells into the conduction band continuum leading to prospective current density components.

The task here is to propose a method of (a) determining photo-carrier concentration δN (in cm^{-2}) in each well, and (b) evaluating thermal currents out of each quantum well. In the process, two recombination mechanisms are mainly important, Auger and radiation recombination. Excess carriers diffuse along the growth direction of the device, in a way dictated by the solution of the diffusion equation:

$$\Delta n(x)=n_1 exp(x/L_n) +n_2 exp(-x/L_n)+n_3 exp(-ax) +n_4 exp(-ax/2) \quad (1)$$

where the coefficients include all the device parameters, L_n is the diffusion length of the electrons, a is the absorption coefficient. The last term in (1) includes the loss effects due to Auger and radiative recombination. The first two terms are simply the homogeneous solution of the diffusion equation, and the rest (3^d and 4th) are its particular solutions (the non-homogeneous part of the diffusion equation is split via partial fractions and two linearly independent particular solutions are found that are of the type $n_3\, exp(-\alpha x)$ and $n_4\, exp(-\alpha x/2)$).

P- and n- regions (of the pin structure) are considered at moderate doping levels, while, in the middle region, *only* quantum wells are to be kept at low background doping levels. Distances from well to well are selected to be large enough so that tunneling may be neglected. The total length of the device is W, and between x_j (end of p-region) and $x_j + L_i$ (end of intrinsic region) various multiple successive layers are assumed to exist. The *p*- and *n*- regions have lengths x_j and $W-(x_j+L_i)$ respectively, where excess carriers develop under illumination as well (not treated here). Typical designs consider, 500 nm repeat distances L_R, with 10 nm quantum wells (fully exploiting quantum size effects) and 490 nm barrier layers, at a total length of ten to twenty periods (i.e. 5 to 10 μm final L_i lengths). Such geometry, namely, *p (1μm)/i (5μm-mqw)/n (1μm)* [total device length $W = 7\mu m$] is of interest, and may provide substantial current density values, although separate calculations will be needed to include *carrier re-trapping and scattering*, once the photo-carriers are above the highest conduction band-edge (work in progress). Each quantum well is characterized by a ground state E_1, a conduction band discontinuity ΔE_c and quasi-Fermi level E_F, pinning of which is predicted by the neutrality equation. The conduction band discontinuity ΔE_c determines the minibands, as computed via standard finite-quantum well techniques. Not more than two of such miniband solutions are to be found in each well, while the ground (first) state is taken as the lowest energy level in the integration steps for the current density. Expression (1) provides net (after recombination) photogenerated carriers per unit volume per quantum well *anywhere* in the intrinsic region. Based on (1), integration over the extent of the nth quantum well, will provide total photo-carrier concentration per unit area δN.

Thermionic currents may be evaluated from photo-generated carriers in each

well and this has been shown in the previous section, by means of Eq. (2). From the latter, a number of parameters seem to be vital factors for final current determination. These are (a) quantum well width L_w (b) photo-generated carriers δN (cm^{-2}) (c) temperature (as $T^{3/2}$) (d) ground state ΔE_1, depending on L_w and (e) quasi-Fermi level position, relative to the conduction band of the low-gap material. Negligible current density values are obtained at intrinsic n_d levels (nA/cm^2), but appreciable currents seem to be feasible above 10^{10} cm^{-3} doping levels, such as 1 to $8mA/cm^2$ predicted (per well) for three representative temperatures (–10, 27, 40 ^0C respectively). Thus at room temperatures, quantum well doping of the order of $5x10^{11}$ cm^{-3} could lead to 4.5 mA/cm^2/well, in the neighborhood of 30^0C, and 4 mA/cm^2/quantum well at $–10^0C$. The computations include a *net* photogenerated concentration of 10^{12} cm^2, with quantum well width of 100A. For a representative variation of L_w from 10 to 100A, current density values vary from 0.45 mA/cm^2 to less than 0.9 mA/cm^2 per GaAs layer. This is done at three different temperatures (-10C, 27C, 40C), and at fixed doping (10^{11} cm^{-3}) and photo-carrier concentration (10^{12} cm^{-2}). For instance, 100A quantum well widths, ensure 0.8 mA/cm^2/quantum well thermal current densities at –10C temperatures (note that L_w determines the value of the ground state in the finite quantum wells. Wide quantum wells ensure increase of thermal current density values, since (as seen in (2) the first exponential factor $exp(-\Delta E_1(L_w(,\Delta E_c)/kT)$ increases with wider quantum well widths. Thermal current variations are depicted against photogenerated carrier concentration δN as obtained from (1), at room temperature, at fixed intrinsic region doping at 10^{11} cm^{-3}, and with 100A quantum wells.

Note that (a) δN does not exceed 10^{12} carriers per unit area (cm^{-2}), (b) calculations in this communication are strictly performed for the nth quantum well, and do not include contributions from neighboring ones. Optimizing, current density values may reach up to $8mA/cm^2$/quantum well, before any trapping or scattering, indicating that a relatively large number of quantum wells would compensate for losses in the transport process.

4 Potential barrier doping

Generally, thermionic current densities may be computed from the fundamental formula derive in [2, 5,6,7]. The formula includes (i) quantum well thickness L_w (ii) quantum well impurity concentration $\delta N(cm^2)$ (iii) temperature as $T^{3/2}$ (iv) ground state miniband in a quantum well and (v) the activation energy exponential factor as follows:

$$J_{th} = B^*(L_w)(\delta N(cm^2))(T^{3/2}) \; exp[E(1)/kT] exp[(E_{c1}-E_F)/kT] \quad (2)$$

where the pre-factor B^* in (2) is a constant and equal to 1.46 $mA/cm/^oK^{3/2}$. Typically, photogeneration from the intrinsic region (incident photon flux levels $10^{17}cm^{-2}$) generates 10^{12} cm^{-2} thermally escaping carriers out of the quantum wells and in the conduction band continuum. At room temperature, for 10nm wide quantum wells, without barrier doping, expression (2) predicts small currents per quantum well, and of the order of micro-amperes(10^{-6}A), since the second exponential factor in (2) is dominated by a large activation energy (700meV). Based on results from [1], light doping of barriers (AlGaAs layers

at 10^{14} - 10^{15} cm^{-3} are expected to cause a 15% reduction of the activation energy from the mid-gap intrinsic value $E_{gGaAs}/2$=710meV, down to 600meV. This means that thermally generated current densities (see (2)) may reach values near 0.277mA/cm^2 out of each well. It becomes clear that light doping of the potential barrier material is of great advantage in designing photo-devices, because the fermi energy is controlled by such doping. Thermionic currents (due to carriers escaping from quantum wells) increase dramatically to fractions of mA/cm^2. The latter effect is not affected by impurity scattering as long as doping levels are kept below intermediate values (less than $10^{17}cm^{-3}$). Further improvements can be succeeded by introducing superlattice structures in the window region, where (a) widening of the gap via higher band gap material and (b) superlattice-like succession of layers may lead to fermi level control beyond the mid-gap as well. In fact, calculations have shown that at moderate doping levels (10^{17-18} cm^{-3} donor atoms concentrations) fermi energies get pinned at 0.15 eV below the conduction band of the low-gap material. Such fermi level pinning at the beginning of the device, causes a relocation of fermi levels in the intrinsic region (under thermal equilibrium), and hence an increase in activation energy by another 10% may increase the currents to several mA/cm^2 in the intrinsic region as well. Controlling the widths of the potential barrier layers in the window layer, may have a positive effect on activation energies: a 50 A barrier-layer, at room temperature may cause fermi level pinning such that activation energy becomes of the order of 0.08-0.1eV. This in effect will reduce the activation energy even further, so that thermal current densities increase even further. Such results lead to the following improved design steps for consideration:

(a) introduction of an AlGaAs-GaAs superlattice region in the window layer with potential barrier layers (instead of single GaAs)
(b) incorporation of a superlattice structure in the intrinsic region of the p-i-n device
(c) moderate doping of the potential barrier layers in the window region
(d) low doping of the quantum wells in the intrinsic region

Based on such design considerations, overall compromise of fermi level pinning takes place above mid-gap levels, thus leading to appreciable net thermionic current densities from the quantum wells.

5 Conclusions

Improvements on collected current density values are possible in p-i-n photovoltaic devices, when quantum size effects are taken into consideration. Typically, bulk p-i-n devices with high collection efficiency are made out of GaAs layers comprising the three regions of the latter devices. Great improvements are predicted when superlattice structures are incorporated in the window and in the intrinsic regions respectively. Wide gap layers in the side of the device that receives the photon-flux, provide wider window because of higher band-gap. On the other hand, superlattices in the same region reduce the electronic activation energy, thus increasing the population of collected electrons from the p- region. At the same time, fermi levels in the superlattice structures introduced in the intrinsic region (of the same kind as in

the p-region) are pinned at locations above mid-gap, thus leading to improved thermionic current densities from the device as a whole. This is successful when wide quantum wells are introduced which are of low doping (10^{12} cm^{-3}). Thus, high doping of AlGaAs layers in the p-region and low doping of quantum well layers (GaAs) in the i-region, are shown to lead to appreciable currents out of the quantum wells. Another advantage of such a design adoption is that the method can be generalized to devices grown out of other lattice-matched materials. Interest, in addition to the GaAs-AlGaAs combination discussed in this communication, is focused on (a) Silicon-based photovoltaic devices, where silicon is the wide-gap material and germanium is the low gap material. 18% collection efficiencies [space applications] of the latter (not as high as those of GaAs-AlGaAs in excess of 25%) are important tradeoffs when costs of fabrication are included in the total process of mass production of this kind of devices.

References:

[1] AC Varonides et al, Neutrality Equation and Fermi Level Shifting in Selectively Doped GaAs/AlGaAs Superlattices, *Advances in Scientific Computing, Computational Intelligence and Applications, N.* Mastorakis, V. Mladenov, B. Suter, L.J Wang Editors, 2001, pp. 66-75.

[2] E. Aperathitis, AC Varonides et al., Temperature dependence of Photocurrent Components on Enhanced Performance GaAs/AlGaAs Multiple Quantum Well Solar Cells, *Solar Energy Materials & Solar Cells,* Vol. 70, 2001, pp. 49-69.

[3] S.M. Sze, *Physics of Semiconductors,* NY, 1981.

[4] A.C. Varonides, Thermionic Escape of Net Photogenerated Carriers and Current Densities from Illuminated Lightly Doped Multiquantum Well Solar Cells, *International Workshop on Nanostructures in Photovoltaics*, Max Planck Institute, Dresden, Germany, 2001.

[5] Ashcroft and Mermin, *Solid State Physics,* Saunders College, 1976.

[6] D.K. Ferry, *Semiconductors*, Macmillan, 1991.

[7] K. Hess, *Theory of Semiconductor Devices,* IEEE Press, 2000.