Gains in Activation Energy from Quasi Fermi Splitting, In Selectively Doped MQW Solar Cells

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Abstract: - Illumination of a Multiple Quantum Well (MQW) solar cell, affects the Fermi level position in the gap, directly under the conduction band of the narrow gap layer. In this communication, we explore Fermi level shifting and splitting in these structures. The neutrality condition is examined in terms of (a) availability of carriers (b) carrier confinement (c) escaping carriers (d) doping levels (e) layer width and (f) Fermi level dependence on doping and illumination. We conclude that short circuit currents and open circuit voltage are seriously affected.

Key Words: - Quantum wells, Fermi level, solar cells, open circuit voltage, short circuit current.

1 Introduction
Low dimensional optical devices are ideal probes for the study of excess carriers in quantum wells. The latter are regions where quantum size phenomena become important, because they are essentially traps of excess electrons.

Optical devices or optical heterostructures offer two advantages over their bulk counterparts: (a) they provide wider optical gaps, expanding the spectrum to shorter wavelengths and (b) they reduce recombination through mass separation: pre-existing electro-static separate electron-hole pairs (in the conduction band and the valence band respectively). This latter phenomenon is more accentuated in reduced dimensionality structures. Typical examples are GaAs and its Alloys: GaAs-AlGaAs (at several Al percentages). In solar cells; they provide higher short circuit currents (at least the III-V ones).

2 The neutrality condition
The concentration of electrons bound in donor atoms can be estimated by ignoring electron-electron interactions. The mean number of electrons is [1,2,3]:

\[ n_d = \frac{N_d}{1 + \exp(\frac{E_d - E_F}{2})} \]

(1)

Where, \( E_d \) is the donor level of energy in a sample with \( N_d \) (cm\(^{-3}\)) donor atoms and \( E_F \) is the “Fermi” energy or chemical potiential. For an n-type sample (\( N_d > N_a \)), electrons distribute themselves in such a way that overall charge neutrality is sustained.

\[ n_c + n_d = (N_d - N_a) + p_v + p_a \]

(2)

The number of conduction and donor electrons at some temperature \( T \) increases over the \( T=0 \) state by the number of holes in the valence band (\( p_v \)). This is the neutrality condition, which allows one to locate the Fermi level at any temperature. In a multi-layered structure consisting of \( N \) repeatable periods, each of width (d) equal to the sum of the potential barrier width (\( d_1 \)) and the quantum well width (\( d_2 \)). Conduction carriers come from the donor sites in the gap of the layer doped with donor impurities. The role of such donor atoms is to raise the Fermi level

Nomenclature:
\( \Delta E_c = \) conduction band difference
\( E_{c2} - E_{d2} = \) donor shallow levels
\( d_1, d_2 = \) low and wide gap width
\( N_{d2} = \) donor concentration
\( N = \) number of periods
\( \gamma_{0,1} = \) miniband width
\( \Delta E = \) minibands (from the bottom of the QW)
\( \Delta E_{CF} = \) \( E_c - E_F \) (activation)
closer to the conduction band of the lower gap material. More free electrons spill into neighboring quantum well sites increasing the electron population and reducing the gap between the conduction band and Fermi energy, and since conductivity \( \sigma = \sigma_0 \exp(-\frac{E_c - E_F}{kT}) \) the transport properties of solar cells are enhanced. While conduction is possible because of excess carriers from the donor sites, neutrality requires that the electrons (per volume) contributed by donor atoms be equal in numbers with the carriers left at the donor levels, plus the carriers that remain in the quantum wells, plus the conduction band free carriers. This is summarized in the following expression (2 refers to the wide gap and 1 to low gap layer):

\[
n_{d2}(NV_2) + n_w(NV_1) + V_T \int dE g_{3d}(E) f(E) \]

\[
= N_{d2}(NV_2) \tag{3}
\]

Where \( n_{d2} \) is the electron concentration due to donor atoms, \( V_1 \) and \( V_2 \) are the volumes of layers 1 and 2, \( V_T \) is the total volume of the sample (the solar cell itself), \( N \) is the number of periods of the superlattice, and \( N_{d2} \) is the donor concentration in layer 2 (AlGaAs). \( \Delta E_c \) is the conduction band discontinuity, \( g_{3d} \) is the bulk density of states (DOS), and \( f(E) \) is the probability distribution of the electrons (Fermi-Dirac or Maxwell-Boltzmann). Since \( V/V_T = d/(N_d) \), expression (3) becomes:

\[
n_{d2} \left( \frac{d_2}{d} \right) + n_w \left( \frac{d_1}{d} \right) + \int dE f(E) g_{3d}(E) \]

\[
= N_{d2} \left( \frac{d_2}{d} \right) \tag{4}
\]

### 3 Carriers in QW’s

Carriers in the quantum wells are expressed via similar integrals as in (3):

\[
n_w(T) = \int dE g_{2d}(E) f(E) \tag{5}
\]

Where the DOS in (5) is 2-dimensional:

\[
g_{2d} = \left( \frac{m^*}{\pi \hbar^2} \right) \sum k_z \Theta(E - E(k_z)) \tag{6}
\]

Where Theta is the step function, and \( k_z \) is the wave-vector of the III-V alloy in the growth direction according to the tight binding theory. The energy dispersion relation is then:

\[
E(k_z) = E_n + 2\gamma_n \cos(k_z d) \tag{7}
\]

Assuming a Maxwell-Boltzmann distribution function for the \( f(E) \) probability, and integrating (5) over the widths of the minibands in the quantum wells, we obtain:

\[
n_w(T) = 4\Gamma_o \exp \left( -\frac{\Delta E_r^0}{kT} \right) \exp \left( \frac{\gamma_o}{kT} \right) \sinh \left( \frac{\gamma_o}{kT} \right)
- 8\Gamma_o \exp \left( -\frac{\Delta E_r^0}{kT} \right) \exp \left( \frac{\gamma_o}{kT} \right) \sinh \left( \frac{\gamma_o}{kT} \right)
+ 10\Gamma_o \exp \left( -\frac{\Delta E_r^0}{kT} \right) \exp \left( \frac{\gamma_o}{kT} \right) \sinh \left( \frac{\gamma_o}{kT} \right)
+ \ldots \text{[Terms with the 2nd mini-band]} \tag{8}
\]

Where \( \Gamma_o = m^*(kT/\pi \hbar^2)(cm^{-3}) \), and \( \Delta E_r^0 \) is the distance of the miniband from the Fermi level plus the activation energy:

\[
E_0 - E_r = \Delta E_r^0 = \Delta E_0 + \Delta E_{CF}
\]

All quantities in (8) are known parameters based on the geometry of the superlattice, and the exponential factors include the Fermi energy.

### 4 Carriers due to donors and carriers above \( E_{c2} \)

The number of carriers donated by shallow donor impurities is \( [4, 5, 6, 7] \):

\[
n_{d2} = N_{d2} \exp \left( -\frac{E_{c2} - E_F}{kT} \right) \tag{9}
\]

Replacing the difference in (9) in terms of the band discontinuity:
\[ n_{d_2} = N_{d_2} \exp\left(-\frac{\Delta E_{CF}}{kT}\right) \exp\left(-\frac{\Delta E_c}{kT}\right) \]  

(10)

On the other hand, free carriers above the conduction band of the wide gap layer, are simple carriers in the energy continuum in the bulk of both layers in a mqw-solar cell. Namely,

\[ n_e = N_e \exp\left(-\frac{\Delta E_c}{kT}\right) \exp\left(-\frac{\Delta E_{CF}}{kT}\right) \]  

(11)

Where \( N_e \) is the effective DOS of the wide gap material.

5 Activation energy \( \Delta E_{CF} \)

We solve for the activation energy from (4) via (5), (8), (10) and (11):

\[ \Delta E_{CF} = kT \ln \left\{ \frac{\exp\left(-\frac{\Delta E_c}{kT}\right)}{\sinh\left(\frac{\Delta E_c}{2kT}\right)} \times F \right\} \]  

(12)

With

\[ F = \left( \frac{d_1 A}{2d_2 N_{d_2}} \right) + \left( \frac{N_e d_1}{2N_{d_2} d_2} \right) \exp\left(-\frac{\Delta E_c}{kT}\right) \]

And where

\[ \gamma_0 = 4 \Gamma_0 \exp\left(-\frac{\Delta E_0}{kT}\right) \sinh\left(\frac{\gamma_0}{kT}\right) \left[ 3 \sinh\left(\frac{\gamma_0}{kT}\right) - \cosh\left(\frac{\gamma_0}{kT}\right) \right] \]

\[ + \left[ \exp\left(-\frac{\Delta E_0 + 2\gamma_0}{kT}\right) \right] \]

6 QFL’s and illumination

We consider a single quantum well between two layers of wide gap material (potential wells). Typically, this means a GaAs layer in contact with two layers of AlGaAs from left and right. An open-circuited solar cell, under illumination, develops a non-zero voltage in its output. This called the open circuit voltage, which is the most important solar cell parameter. It is because of this voltage, that the device will eventually sustain a current through a load, when applied for production of electricity. The question becomes: what is the effect on the Fermi levels on both sides of the solar p-n junction? Under zero illumination the Fermi levels coincide. This is because the number of carriers from left to right equals the number of carriers from right to left. Note that if \( f_1(E) \), \( f_2(E) \) are the Fermi functions in the two regions, \( g_1(E) \), \( g_2(E) \) the DOS of the two regions, then:

\[ g_1(E) \left(1 - f_1(E)\right) g_2(E) f_2(E) = \]

\[ g_1(E) f_1(E) g_2(E) \left(1 - f_2(E)\right) \]  

(13)

and therefore \( f_1 = f_2 \).

Also, under illumination, open circuit voltage develops, so that:

\[ g_1(E) \left(1 - f_1(E)\right) g_2(E + qV_{oc}) f_2(E + qV_{oc}) = \]

\[ g_1(E) f_1(E) g_2(E + qV_{oc}) \left(1 - f_2(E + qV_{oc})\right) \]  

(14)

From (14) it follows that

\[ f_1(E) = f_2(E + qV_{oc}) \]

Or that

\[ E_{F_2} - E_{F_1} = qV_{oc} \]  

(15)

Expression (15) establishes the fact that under open-circuit condition and under illumination, the solar cell (any solar p-n junction) reacts within neutrality accordingly. First of all, due to open-circuit voltage, the device adjusts to zero currents by splitting the Fermi level into two quasi-Fermi level in regions 1 and 2. This exactly is the meaning of expression (15). On the other hand, illumination causes a further split in the quasi Fermi level of medium 1 (low gap medium). This is due to the fact that as carriers in the quantum wells increase in numbers, the mere quantum event of carrier confinement cause a re-adjustment of the quasi-Fermi level in medium one. Thus, under illumination (a) the Fermi levels split by \( qV_{oc} \) due to neutrality conditions and (b) the quasi Fermi level \( E_{F_1} \) shifts upwards by an amount \( \Delta \mu \) of the order of 12 meV. Thus the overall open circuit
voltage will increase. Figure 1 below depicts the situation: a quantum well and Fermi level behavior.

Figure 1: Three quasi-Fermi levels in the vicinity of a quantum well with its eigen-energy. The total open circuit voltage and the excess Fermi level splitting are shown explicitly.

As seen from Fig. 1 above, the expected open circuit voltage increases by an amount $D_m$, due to quantum size effects. Thus an overall gain is expected as far as open circuit conditions are concerned.

7 Results

The goal in this communication is to show clear improvements in the activation energy of a solar cell with quantum wells in its intrinsic region. Activation energy is the difference in energy between the bottom of the quantum well (hence the conduction band $E_{c1}$) and the actual Fermi energy right beneath it. As seen in Fig. 1, the Fermi energy shifts and splits under illumination. Table 1 below depicts the gain on activation energy.

Table 1: Activation energy without and with Fermi level split due to quantum size effects, in the quantum wells.

<table>
<thead>
<tr>
<th>$d_2$ (Å)</th>
<th>$E_{c1} - E_{F1}$ (eV)</th>
<th>$E_{c1} - E_{F1}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No split</td>
<td>With split</td>
</tr>
<tr>
<td>5</td>
<td>0.260</td>
<td>0.248</td>
</tr>
<tr>
<td>10</td>
<td>0.250</td>
<td>0.238</td>
</tr>
<tr>
<td>15</td>
<td>0.240</td>
<td>0.228</td>
</tr>
<tr>
<td>20</td>
<td>0.245</td>
<td>0.233</td>
</tr>
<tr>
<td>25</td>
<td>0.244</td>
<td>0.232</td>
</tr>
<tr>
<td>30</td>
<td>0.240</td>
<td>0.228</td>
</tr>
<tr>
<td>35</td>
<td>0.220</td>
<td>0.208</td>
</tr>
</tbody>
</table>

Table 2: Activation energy dependence on doping.

<table>
<thead>
<tr>
<th>$N_d$ ($cm^{-3}$)</th>
<th>$E_{c1} - E_{F1}$ (eV)</th>
<th>$E_{c1} - E_{F1}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without QF-split</td>
<td>With QF-split</td>
</tr>
<tr>
<td>$8.65 \times 10^{16}$</td>
<td>0.360</td>
<td>0.348</td>
</tr>
<tr>
<td>$1.47 \times 10^{17}$</td>
<td>0.355</td>
<td>0.343</td>
</tr>
<tr>
<td>$2.35 \times 10^{17}$</td>
<td>0.350</td>
<td>0.338</td>
</tr>
<tr>
<td>$3.88 \times 10^{17}$</td>
<td>0.335</td>
<td>0.323</td>
</tr>
<tr>
<td>$6.39 \times 10^{17}$</td>
<td>0.320</td>
<td>0.308</td>
</tr>
<tr>
<td>$1.0 \times 10^{18}$</td>
<td>0.310</td>
<td>0.298</td>
</tr>
</tbody>
</table>

As seen from Table 2, high doping of the barrier region causes narrower activation energy. The third column of table 2 depicts the final position after the Fermi level split correction. We notice that the activation energy reduces by a net amount of the order of 12 meV. Such reductions cause an increase to conductivity by a factor $\exp(\Delta \mu / kT)$. Thus gains in the activation energy and in the open circuit voltage are expected when superlattices are incorporated in heterostructure solar cells.

8 Conclusions

When superlattices [8,9] are used in solar cells, the activation energy is the difference in energy between the bottom of the conduction band and the Fermi level (see Fig. 1). This study has shown that the Fermi level depends on (a) the geometry of the device (this means the layer characteristics and (b) on the doping levels, as seen from Table 2. In both cases (as in Table 1, 2) the activation energy reduces. Our general conclusion is that excessive doping of the wide gap layer and gradual increase of the of the width of the potential barrier produce a Fermi level
split which is equal to the open circuit voltage. Furthermore, the open circuit voltage will increase by the amount of ~12 meV, which produces an even higher open circuit voltage. Losses are found from the fact that temperature increases cause a reduction in the activation energies. We attribute this fact to the role of high temperatures: the higher the temperatures the more scattering expected, and hence more losses.

9 References