High Open Circuit Voltage of MQW Amorphous Silicon Photovoltaic Structures

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Abstract: - The maximum theoretical open circuit voltage of a solar cell is set by its built-in voltage. For amorphous silicon p-i-n cells, the position of the Fermi levels in the p-and n- contact regions are on the order of 0.4 eV and 0.2eV from their respective band edges, limiting the built-in voltage to E_g - 0.6eV. We propose replacing the p- and n - regions by superlattices, in which the Fermi levels in the wide gap barrier regions are, on an absolute scale, closer to the valence band or conduction band edges of the low gap material (a-Si:H), than the values indicated above. In order for the p - and n- superlattices to yield a larger build-in voltage, the density of states in the doped wide band materials must be much greater at the Fermi levels than that of the undoped low band gap quantum wells. To accomplish this, the wide gap material must be heavily doped and have effective tails much wider than that of the undoped low band gap material. For the n-region superlattice the barrier must be in the conduction band, hence we propose a -$Si_{1-x}C_x$: H and a -Si:H: For the p-region superlattice the barrier must be in the valence band, and we propose a -$Si_{1-y}N_y$: H and a -Si:H.

Keywords: - Superlattices, Quantum wells, amorphous silicon, solar cells,

1 Introduction

While impressive gains in the efficiency of amorphous silicon based solar cells have taken place in recent years, the gains have been accomplished by improvements primarily in short circuit current and fill factor, while the open circuit voltage has been essentially pinned in the ~ 0.9V ± 0.04V range. Several factors may affect the open circuit voltage of a p-i-n solar cell; recombination in the low field portion of the i-region, recombination near the n-i or p-i interfaces, and recombination in the n- or p-region are the basic mechanisms. However, no matter how one reduces these effects, the maximum open circuit voltage of a single junction cell is limited to its built-in voltage. In the currently produced amorphous silicon p-i-n cells, the Fermi levels in the p-region is ~o.4 e V above the valence band, and in the n-region ~ 0.2 eV below the conduction band. This produces a built-in voltage of E_g-0.6eV ~ 1.1eV. The reason for the limits in E_c-E_f and E_f-E_v, is that the nature of tail states and defect states in amorphous material is such, that increased doping produces additional defects that prevent the Fermi level from moving closer to the band edges.

Work in crystalline and amorphous superlattices [1-10] has opened the possibility of tailoring the n- and p- contact regions in such a way,

that the Fermi level position in these regions can move closer to their band edges, resulting in a higher built-in voltage, while still providing adequate conductivity. The basic idea is that in an n-type superlattice the wide band material has its *Fermi level higher on an absolute scale than the neighboring low band gap material even* if the low gap material were optimally doped. While having a higher Fermi level on an absolute scale, the wide band gap material would not be a suitable contact by itself, since its value of E_c- E_F is greater than that of the low gap material, and hence would have lower conductivity. However, in a superlattice the carriers can tunnel through the wide gap material if it is thin enough, and hence if its Fermi level can be made to dominate the superlattice, a larger built-in voltage can be obtained, without loss of sufficient conductivity.

For a p-type superlattice contact the valence band of the wide gap material must lie below that of the low gap material, while for the n-type case the conduction band of the wide gap material must lie above that of the low gap material. In order for the wide gap material to determine the Fermi level position in the superlattice, and make the superlattice Fermi level essentially that of the wide gap material, the density of states in the wide gap material at the common Fermi level must be greater than that of the low gap material at the common Fermi level. Since $N(E_F)$ for n-type material is

$$N(E_F) \sim N(0)\, e^{(E_c-E_F)/kT^*}$$

Where N(0) is the density of states in energy at the conduction band edge, and kT* is the width of the band tail states assumed to be exponential. The condition for wide-gap (WG) and lower-gap (LG) is that:

$$(E_c - E_F)_{WG} > (E_c - E_F)_{LG},$$

Which in turn requires that either

$N(0)_{WG} >> N(0)_{LG}$ or that

$(kT^*)_{WG} > (KT^*)_{LG}$

Since it is well known that heavy doping widens the effective value of (kT*), one way to achieve the needed condition is to heavily dope the wide gap material, while leaving the low gap material undoped or lightly doped.

Since, we also want to preserve low resistance paths through the superlattice contacts, the thickness of the wide gap barrier material should be small, and in order not to increase the effective band gap of the contact region enough to make a barrier for the carrier, the low band gap region width should be chosen appropriately. The remainder of the paper treats the superlattice calculations to determine the design tradeoffs. We note that n - and p - superlattice contact regions have been used and have resulted in some cases in improved open circuit voltage [11], and in others in increased current [12]. To our knowledge no one has attempted to utilize the superlattice for the purpose proposed in this paper.

2 Relation of Fermi Levels to V_{OC}

At open circuit voltage conditions the diode current of the p-i-n structure equals the short circuit current, neglecting any non-superposition effects. The diode current depends strongly on

where the injected carriers recombine and how they recombine. In a conventional p-n junction crystalline silicon solar cell, the carriers generated by light and those injected in forward bias are essentially non-interacting and the dark diode current and short circuit, I_{SC}, simply add via the relation,

$$I = I_{dark} - I_{sc} = I_s(e^{qV/kT} - 1) - I_{sc} \quad (1)$$

Setting I = 0 yields the open circuit voltage

$$V_{oc} = nkT\ln(1+(I_{sc}/I_s)) \quad (2)$$

Where I_S is the dark saturation current and n the diode ideality factor; n~1 in good cells. For an ideal material (n = 1) one can write for I_S per unit area J_s:

$$J_s = J_o\, e^{-qVbi/kT} \quad (3)$$

Where q is the electronic charge, V_{bi} is the built-in potential, and J_o is device parameter-related pre-factor. If one side of the junction is much more heavily doped we can write

$$J_s = qN_H\,(L_H / \tau_H)\exp[-(E_g-\delta_L)/kT] \quad (4)$$

Where N_H is the equivalent density at the band edge of the heavily doped carrier, L_H and τ_H are the diffusion length and lifetime of the heavily doped carrier on the lightly doped side of the junction, and δ_L the Fermi level separation from the band edge in the lightly doped material (note that $qV_{bi} = E_g - \delta_n - \delta_{p.}$ An expression for V_{oc} [15] for the ideal material is in the limit $J_{SC>>}J_S$:

$$qV_{oc} = (E_g - \delta_L) + kT\ln[(J_{sc}\,\tau_H)/(qN_H\,L_H)] \quad (5)$$

with typical values of J_{sc} = 30mA/cm^2, while $qN_HL_H / \tau \sim 10^3$-10^4 A/cm^2. For an amorphous silicon based p-i-n solar cell, recombination of the electrons and holes injected in forward bias can take place in the i-region or at interfaces. Assuming that the position of the valence band edges of the p- and i- regions are the same (with suitable material selection), and that the conduction band edges of n- and i- region are the same, one finds that if $\delta_n < \delta_p$ interface recombination at the p-i interface dominates [12, 14] and J_d is given by:

$$J_d = qN_c\, S \exp[-(E_g - \delta_p)/kT] \exp(qV/kT) \quad (6)$$

Where S is the recombination velocity at the p-i interface. From this one finds V_{oc}:

$$qV_{oc} = E_g - \delta_p + kT\ln[J_{sc}/qN_cS] \quad (7)$$

For typical values j_{sc} = 15 mA/cm^2, $N_c = 10^{18}$/cm^3, S = 10^5 - 10^6 cm/sec, V_{oc} = 0.88 - 0.94V, which agrees with the range seen in good cells.

3 E_F in amorphous Silicon Superlattices

To calculate the Fermi level-in an n-type superlattice we need to take into account, the donor levels, the electrons in the conduction bands, the electrons in the quantum wells, the electrons in band tail states, and the electrons in dangling bond states. To properly simulate the behavior observed in a -Si: H and its alloys, we require that for every donor impurity incorporated, beyond a given value, a dangling bond state or tail state is created that lies below the maximum position of the Fermi level in the

material. This results in pinning the Fermi level of the material at some maximum value. To estimate the conditions and tradeoffs, consider a low temperature case, where only the density of states needs to be taken into account, and the calculations can be done analytically. For finite temperatures the calculations have to be done numerically [16]. For n-type material the conduction band tail states are given by:

$$g_c(E) = N_{oc}\, e^{-(EC - E)/kT^*}$$

Where N_{oc} is the density of states at the conduction band E_c. Assume that the wide gap material is doped and would have a Fermi level of E_{F2} and a tail state width, kT_2*. The narrow gap material is assumed undoped, and has fermi level at E_{F1} and a tail state kT_1^*. Assume also that, on an absolute scale, that $E_{F2} > E_{F1}$ i.e. suppose E_{F1} = 1.15eV above the assumed common value of E_v, and E_{F2} = 1.65eV above E_v, or 0.55 eV below E_{C2}. Since the total number of electrons is conserved, at T=0 electrons leaving material 2 will fill states in material 1, until the Fermi levels are equal. We can integrate $g_1(E)$ from E_{F1} to E_F to calculate the states filled in the low gap material, and $g_2(E)$ from E_F to E_{F2} for the states emptied in the wide gap material, after the integrations,

$$N_{oc2}\, d_2\, kT_2^*$$

$$x\{e^{-(E_{c2} - E_{F2})/kT_2^*} - e^{-(E_{c2} - E_F)/kT_2^*}\} =$$

$$N_{oc1}\, d_1\, kT_1^*$$

$$x\{e^{-(E_{c1} - E_F)/kT_1^*} - e^{-(E_{c1} - E_{F1})/kT_1^*} \qquad (8)$$

Where d_2 is the width of the wide gap material and d_1 that of the low gap material. What this equation reveals is that the value of E_F could be determined. The only way to shift E_F upward significantly is for kT_2* to be such that:

$$e^{-(E_{c2} - E_{F2})/kT_2^*} > e^{-(E_{c2} - E_F)/kT_1^*}$$

(if $T_1^* = T_2^*$, $d_2 = d_1$, and since $E_{c2}-E_F \sim E_{c1} - E_{F1}$)

Which requires that

$$E_{c1}–E_F = (E_{c2}–E_{F2})\ (T_1^*/T_2^*) \qquad (9)$$

Note that E_F cannot exceed E_{F2}. Hence, we see that a large density of states at the Fermi level is needed in the wide gap material, if it is to determine the Fermi level of the superlattice. Typical values of $E_{c2} - E_{F2}$ are 0.55eV, and thus for E_F to be nearly E_{F2}, the temperature ratio must be such that

$$T_1^*/ T_2^* = 1/4$$

So that $E_{c1} - E_F$ = 0.1eV.

In this case:

$$E_{c1}–E_F = (T_1^*/T_2^*)\ (E_{c2} – E_{F2})-$$

$$kT_1^* \ln\{(N_{oc2}\, d_2\, T_2^*) / (N_{oc1}\, d_1\, T_1^*)\} (10)$$

For a p-type material similar considerations may hold, but for holes. The valence band of the wide gap material must be below that of the narrow gap material. Fig. 2 illustrates the overall structure of a p-i-n cell, with both n- and p- region superlattices

4 Other Properties

While control of the Fermi level position of the superlattice contacts is key to a possible increase in V_{OC}, the effective optical band gap can be controlled by the width d_1 of the well regions. Hence, the amount of absorption in an n- or p- superlattice can be controlled. However, a more important property is the conductivity through the superlattice. Expressions for the parallel and perpendicular conductivity of an n-type superlattice are:

$$\sigma_{par} \sim \exp[-(E_c-E_F)/kT]\exp(-E_o/kT) \quad (11)$$

and

$$\sigma_{vert} \sim t^2 \exp(-E_o/kT)$$

with

$$t^2 \sim (kT) \exp\{-2d_2[(\Delta E_c-E_o)/\beta] \quad (12)$$

Where E_o is the first allowed level in the quantum well, ΔE_C the band edge offset, and β quantum mechanical constant. Since $E_0 \sim d_1^{-2}$, its value can be reduced by widening the wells. However, for $\sigma_{vertical}$, which is important to the series resistance of the solar cell d_2, and ΔE_C are the key parameters. ΔE_C is controlled by varying the carbon content in the a-$Si_{1-x}C_x$: H alloys; and for the analogous p- superlattice ΔEv is controlled by the nitrogen in a-$Si_{1-y}N_y$: H alloys. Other combinations of constituents are also possible for both n - and p- superlattices. The considerations indicated above, make it clear that the effective optical band gap and transport properties of a superlattice can be adjusted to make it a practical contact for p - i - n solar cells.

4 Summary

It has been proposed that the built-in voltage of a p-i-n amorphous silicon solar cell can be increased by use of appropriately designed superlattice contact regions. The conditions necessary to achieve a higher built-in voltage are that the density of stated at the fermi level of the wide gap material exceed that of the low gap material. The most obvious parameter for this purpose is T*, which can be increased by heavy doping. Other factors are the superlattice optical gap widening and the superlattice geometry. A major uncertainty is whether the fermi level of the wide gap material can be forced to exceed the fermi level of the narrow gap material. Possible superlattices could be based on a-$Si_{1-x}N_x$:H/a-Si:H layers or a-$Si_{1-x}Ge_x$:H/a-Si:H, but in general the position of the fermi level is not well known.

5 Conclusions

Our conclusions are

(i) the concept of using n- and p-type amorphous silicon based superlattices to increase the built in voltage in p-i-n solar cells is valid

(ii) the fermi levels in the doped wide gap barrier regions have to be, on an absolute scale, closer to the valence band or conduction band edges of the low gap material alone

(iii) the density of states of the wide gap material at the final common fermi level has to be much greater than that of the low gap material. This requires a large kT*, which can be accomplished by heavy doping of the wide gap material.

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