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Amorphous Silicon Superlattice Solar cells

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Abstract - Amorphous silicon/alloy superlattices provide advantages in solar cell design, such as (a) effective band-gap widening (b) effective mass separation (c) increased open-circuit voltage. The latter increases via Fermi level control, due to p-doping of potential barriers, pushing EF towards the valence bands, with simultaneous widening of the effective band gap, thus leading to potentially higher collection incident wavelengths. The density of gap states in the heavily doped layer is modeled as an exponential whose parameter kT* can be varied by the doping concentrations, while its activation energy saturates at some value. This communication provides (i) a general formulation of the problem at finite temperatures as well as numerical results for specific realizable contacts (ii) detailed treatment of gap states (iii) the neutrality condition (iv) a relation between Fermi level position and open-circuit voltage in the nitride region (superlattice p-region). For a p-(a-SiN: H/a-Si: H)-i (a-Si: H)-n (a-Si: H) sample, we compute the Fermi level position relative to the a-Si: H valence band edge. For low and wide gap thin layers of the order of 2.5 to 3.5 nm, open circuit voltage values are predicted in excess of 1.05 V, and efficiencies are predicted in excess of 12%.

1 Introduction

Amorphous superlattices composed of two amorphous semiconductors such as a-Si:H/a-SiC:H are promising probes for overall solar cell improvement. This is due to the fact that such novel devices essentially combine advantages of multilayered structures and low fabrication cost as it has been established in the industry of the amorphous silicon. One of the advantages of superlattice-based devices is the existence of mini-bands in the conduction bands of the media involved. Thus quantization of carrier motion leads to discrete energy eigen-solutions within the quantum wells. On the other hand, the Fermi level controls the properties of the solar cell, thus predicting its position in the gap of the compositional amorphous silicon-based superlattice. It is well established that the Fermi energy is pinned in the gap and on the other hand, there is a possibility of shifting it towards the band edges, namely, upwards to the conduction band in the n-region of the device, and downwards to the top of the valence band of the p-type structure. Note that degeneracy is unlikely since high doping levels do not tend to change the activation energy as abruptly as in the case of the crystalline semiconductors. The latter are clean materials with no dangling bonds whatsoever. In an amorphous semiconductor instead, the impurities introduce more and more defects, and as a result, the Fermi level gets

pinned well below the edges. In a-Si: H for instance, the distance of the Fermi level E_F from the conduction band edge is of the order of 0.2 eV for an n-type sample, while for a p-type sample E_F is 0.4 to 0.6 eV away from the valence band. A superlattice will cause a shift of the Fermi energy to the edges (of each region) thus improving the open circuit voltage. We propose here heavy doping of the wide-gap material and low doping of the low-gap material. The density of gap states in the heavily is modeled as an exponential whose width parameters kT* can be varied by the doping concentrations, while its activation energy saturates at some value. The proposed increase in built-in and open circuit voltages occurs if the position of the Fermi level in the wide gap material is closer to the relevant band edge of the narrow gap layer, than one could succeed with the narrow gap layer alone. At the same time one could not utilize just the wide gap material as a contact layer by itself, since the value $E_c - E_{Fn}$ or $E_{Fp} - E_v$ is greater than that of the lower band gap material, and thus would have a very low conductivity. In addition, a barrier at the interfaces for carrier collection would really exist. Therefore, a superlattice design offers the possibility of carrier tunneling through the wide gap material (thin layers involved, hence quantum size effects are feasible) and hence a larger built-in voltage is obtained without loss in conductivity. Section 2 of this communication provides the general formulation of the problem at finite temperatures as well numerical results for realistic contact layers, section 3 deals with the neutrality equation and the relation to open circuit voltage. Section 4 contains numerical results for open circuit voltage, transverse and longitudinal conductivity, and a series resistance for various properties of the superlattice compositions.

2 Gap states distribution in amorphous semiconductors

In superlattice structures the density of states (DOS) is a staircase (constant and 2-dimensional per layer) following the 3-dimensional pattern of DOS. In amorphous materials the neutrality condition, in thermal equilibrium, needs modification. In addition to the "staircase" behavior of the DOS, another distribution of states exists in the gaps of both semiconductors involved. The gap states may contain a number of trapped carriers. The concentration of trapped electrons n_t and holes p_t, is typically found from the following expressions:

$$n_t = \int dE f(E) g_c(E) \qquad (1)$$

$$p_t = \int dE (1 - f(E)) g_v(E) \qquad (2)$$

Where the Fermi-Dirac occupation probability is f(E) and where the gap states (/eV/cm^3) for both kinds of carriers are:

$$g_c(E) = N_{OC} e^{-(E_c - E)/kT_c^*} \qquad (3)$$

$$g_v(E) = N_{ov} e^{-(E - E_v)/kT_v^*} \qquad (4)$$

The temperature factors in the exponentials represent the width of the distribution of states in the gap and are the same for valence and conduction band tail states.

3 Neutrality condition

The neutrality equation must be modified appropriately to include the existence of the trapped carriers. At T=0, electrons leave the material with higher Fermi energy (material 2 or wide gap semiconductor) and they fill states in medium 1 (medium 1 or low gap material), in order to satisfy the requirement for constant Fermi levels. The number of transferred electrons and the position of the Fermi level may be found ($T \rightarrow 0$, $f(E) = 1$) from the following condition:

$$d_2 \int_{E_F}^{E_{F2}} dE g_{C2}(E) = d_1 \int_{E_{F1}}^{E_F} dE g_{C1}(E) \quad (5)$$

Where $d_{1,2}$ are the widths of media 1 and 2 respectively, and where the DOS functions are:

$$g_{C2}(E) = N_{OC2} \exp(-\frac{E_{C2} - E}{kT_2^*}) \quad (6)$$

$$g_{C1}(E) = N_{OC1} \exp(-\frac{E_{C1} - E}{kT_1^*}) \quad (7)$$

As the temperature increases, one has to include in (5) the temperature dependence through the Fermi-Dirac distribution. One has to include (a) trapped carrier concentrations n_t for both materials (b) carriers trapped in the quantum wells n_t (c) carriers contributed by the donor impurities n_{d2} (d) free conduction electrons n_c (e) transferred electrons from medium 2 to medium 1, due to the band offset ($E_{c2} - E_{c1} = \Delta E_c$). Expression (5) is generalized as follows:

$$(\frac{d_1}{d})\left(n_w(T) + n_{t1} + \int_{\Phi_1}^{\Phi} dE f(E) g_{C1}(E) \right) + \int_{\Delta E_C}^{\infty} dE f(E) g_{3D}(E) +$$

$$(\frac{d_2}{d})(n_{d2} + n_{t2}) = \left(N_{d2} + \int_{\Phi}^{\Phi_2} dE f(E) g_{C1}(E) \right)\left(\frac{d_2}{d} \right) \quad (8)$$

Where ΔE_c is the band offset, $d=d_1+d_2$ and Φ, Φ_1, Φ_2 are the Fermi levels (finalized and initial ones in the two media). DOS in 3-dimensions is g_{3D} and refers to electrons in the bulk, past the band offset. Effective masses need to be taken into account of course due to the nature of the materials involved (amorphous against crystalline materials). The best fitted values for electronic effective masses are $m^* = 0.4m_o$ for a-Si and its carbon – based alloys. Parameters important for deice design are (a) conduction band offset (b) subband widths: each solution in the quantum wells forms a band, hence tunneling is possible. Eigen-solutions depend on the geometry of the structure, namely, widths of both barriers (Si-alloy) and quantum wells (a-Si). The latter may offer one or two quantum states in the quantum well, depending on the actual width chosen. The structure in mind is as follows: in the n-region of the p-i-n structure, there is a multiquantum well where

the high band gap material is doped with donor impurities. The lower gap material is left undoped while both layers are grown sufficiently thin in order for (a) quantization and (b) negligible band bending to occur. A similar situation is adopted at the p-side of the device. Charge neutrality will determine the final Fermi level position at equilibrium. The p (or p^+) region includes a succession of wide gap (a-Si nitride alloy) and narrow gap (a-Si). The reason for selecting nitride alloys is that one needs the barrier to be in the valence band, since in this case E_F will be shifted to lower positions toward the top of the valence band. The latter situation would ensure higher built-in voltage. For the nitride region we propose a superlattice of a-$Si_{0.8}N_{0.2}$: H ($\Delta E_v = 0.21$ *eV* and negligible ΔE_c), hence with a flat conduction band. In reality there is a 30meV conduction band discontinuity, but we ignore the effect of very shallow quantum wells and consider them as a flat band. In either region, where superlattices are grown, the Fermi level will be at least at the location Φ_1 (= E_{F1}) of layer 1 (low gap a-Si: H). Any other position of the finalized Fermi level will result in open circuit voltage improvement, simply because the latter depends on the difference of the quasi Fermi levels in the two regions. For the p-type side, neutrality dictates that:

$$d_2 \int_{\Phi 2}^{\Phi} dE g_{v2}(E) f(E) = d_1 \int_{\Phi}^{\Phi 1} dE g_{v1}(E) f(E) \quad (9)$$

Where the probability is the *Maxwell-Boltzmann* distribution function for holes, and where hole-quantization causes no major effects in the neutrality condition. In addition, the mobility of the holes is much lower that the electrons' mobility, so that tunneling for holes is very unlikely in the p-region. Amorphous silicon carbide superlattice offers upward Fermi level shifting in the n-region. Carbide alloys of silicon offer abrupt interfaces and when they are combined with lower gap layers of single silicon, in addition, the valence band offset is non-existent (within the experimental uncertainties).

4 Open circuit voltage and the Fermi level

For amorphous silicon based p-i-n solar cells, recombination of the electrons and holes takes place either in i-region or at the interfaces. Since recombination at the p-i interface dominates, one may evaluate the open circuit voltage V_{oc} from the following formula:

$$qV_{oc} = E_g - (E_F - E_v)_p + kT \ln\left(\frac{j_{sc}}{qN_c S}\right) \qquad (10)$$

Where S is the recombination velocity at the interface, j_{sc} is the short circuit current, N_c is the carrier density, E_g is the band gap energy, and $(E_F - E_v)_p$ is the Fermi level position in the gap of the p-type side of the p-i-n device. Typically, $j_{sc} = 15 - 18$ mA/cm^2, $S = 10^5 - 10^6$ cm/sec, $N_c = 10^{18}$ cm^{-3}. As the doping level of the p-type region increases (e.g. B_2H_6 / SiH_4 + NH_3 doping gas ratios from 10^{-4} to 10^{-2}), the Fermi level moves away from the midgap (1.96/2 = 0.98 eV), in other words, the Fermi level of nitride alloy superlattice gradually shifts to the valence band edge as the B content increases.

One may use the conduction band edge of the p^+ - region (silicon/silicon nitride) as the reference energy level, while for the n^+ - region the valence band edges may be taken as the reference energy scale, for the sake of computations. As the bulk level E_{F2} moves away from the midgap of layer 2, the final E_F compromises within the range $\Delta E_F = E_{F1} - E_{F2}$, and it remains to be seen if it can get closer to the silicon valence edge. Silicon-nitrides are good candidates for p-region wide gap superlattice structures. Integration of expression (9) (via expression (4)) leads to the following:

$$\left(\frac{e^{-(E_{F2}-E_{V2})/kT_2^*}}{e^{-(E_{F2}-E_F)/2n_2^*kT_2^*}}\right)\times\left(\frac{e^{(E_{F1}-E_{V1})/kT_1^*}}{e^{(E_{F1}-E_F)/2n_1^*kT_1^*}}\right) \tag{11}$$

$$\times\left(\frac{\sinh\left(\frac{E_{F2}-E_F}{2n_2T_2^*}\right)}{\sinh\left(\frac{E_{F1}-E_F}{2n_1T_1^*}\right)}\right)\times e^{-\Delta E_F/kT}=\left(\frac{1-n_1}{1-n_2}\right)\times\left(\frac{d_1/d_2}{N_{V2}N_{V1}}\right)$$

Where $n_1 = 1/(1-\alpha_1)$, $n_2 = 1/(1-\alpha_2)$, $\alpha_{1,2} = kT_{1,2}^*/kT$, and where $\Delta E_F = E_{F1} - E_{f2}$. From expression (11) we compute the Fermi level at equilibrium and for various parameters. For p-doped experimental values of $E_{C2} - E_{F2}$ (doped silicon-nitride alloys), we compute ΔE_F relative to E_{F1}. Table 1 below shows direct computation results:

Table 1: Fermi level positions, open circuit voltage and computed efficiency gains

$E_{F2} - E_{v2}$ (eV)	$E_F - E_{v1}$ (eV)	V_{oc} (V)	n (%)
0.56	0.512	1.008	10.58
0.46	0.425	1.095	11.49
0.36	0.338	1.182	12.41
0.31	0.294	1.226	13.25

5 Conclusions

This communication addresses the dependence of open circuit voltage on Fermi level position as found in superlattice based amorphous silicon solar cells. We propose a novel solar cell structure where the window is a p-doped superlattice composed of a succession of wide gap and low gap layers of amorphous silicon and its nitride alloys. For the computations we used experimental data on a-Si nitrides with 20% nitrogen concentration against a-Si. Under suitable p-doping of the wide gap layers, we predict increases in open circuit voltage values. The latter, as a basic component of high efficiency gains, leads to collection efficiencies in excess of 12%. Silicon nitrides incorporated in superlattice structures seem to be good candidates for high efficiency amorphous silicon solar cells.

6 References

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