INTRODUCTION

In 1961 Shockley and Queisser first introduced the idea of the detailed balance limit to solar cell efficiency [1]. Their method recognised that in the radiative limit, the photon flux entering a cell minus that re-radiated must be equal to the rate of extraction of charge carriers. This technique has since been extended and refined by various authors: a single junction, detailed balance, computer model [2] predicted that the ideal bandgap for operation under an AM1.5d spectrum should be pinned near 1100nm between at least 30 and 1000 suns due to water absorption features in the solar spectrum. The GaAs band edge (873nm) is therefore lower than desired for optimal efficiency. Unfortunately there are no suitable materials lattice matched to gallium arsenide with band edges close to the required 1100nm. By growing quantum wells (QWs) in the intrinsic region of a p-n device we can lower the bandgap of the cell. The optimum band edge of 1100nm assumes unity above-bandgap absorption. This is a physically unrealistic assumption since even small departures from the stress balancing condition [3] scale up with i-region thickness in the manner of a one dimensional random walk. At thicknesses of around one micron the QW heterostructure starts to relax, forming non-radiative recombination centres which sharply reduce performance. In order to maximise absorption we have grown up to 65 QWs without dislocations [4]. A distributed Bragg reflector (DBR) under the cell also increases absorption by reflecting unabsorbed radiation back towards the QWs. An example quantum efficiency of a quantum well solar cell (QWSC) is shown below to illustrate the level of QW absorption that is currently achievable.

Figure 1. External quantum efficiencies of QWSCs with and without a DBR.

This paper addresses the problem raised by figure 1 as to whether extending the band edge via QWs, is beneficial when the assumption of complete absorption is disregarded.

2 THEORY

The principle of detailed balance is based upon the following assumptions:

- Complete absorption/transmission of above/below bandgap photons.
- All incident photons produce one electron-hole pair and all recombination events produce one photon.
- All the photogenerated charge carriers are collected at the terminals.
- Only radiative inter-bandgap transitions are present.
- The cell emits according to the generalized Planck distribution of emission.
- There are no optical loss mechanisms such as reflection of incoming light.

The goal of this paper is to do away with the first of these statements with particular reference to QWSCs.

The second and third points above imply that the absorptivity is equivalent to the quantum efficiency. In this model we also incorporate a finite front surface reflectivity. We use the formalism of reference [5] as outlined below.

The emission from a semiconductor $b_s$ in photons/nm$^2$/Joule/steradian [6] is given by

**Keywords:** Quantum Well, Multijunction Solar Cell, Modelling
\[ b_s(E, \mu) = \frac{2\mu^2}{h^c e^{(E-\mu)/kT}} - 1 \]  
where \( \mu \) is the chemical potential difference between conduction and valence band populations and \( n \) is the refractive index of the semiconductor. The total radiative dark current can then be written as an integral over surface area, solid angle and energy [5]:
\[ I = q \int \int \int dS \int d\Omega \int dE \alpha(E, \theta, S) b(E, \mu, \theta) d\Omega dS dE \quad (2) \]

We now introduce five further assumptions:
- Absorption is independent of the position that light hits the surface of the cell, \( S \).
- Absorption depends on angle only in that it varies according to the Beer-Lambert law to the path length through the cell: \( \alpha(E, \theta) = 1 - e^{-\mu(E)\cos\theta} \)
  where \( d' \) is the thickness of the absorbing layer and \( \alpha(E) \) is the absorption coefficient.
- The cell is grown on a fully absorbing, index matched substrate.
- \( E-\mu \gg kT \) for all energies above the bandgap. This is a good approximation at room temperature.
- Incident light travels perpendicular to the surface once it has entered the cell, such that the quantum efficiency can be written as \( \alpha(E) = \alpha(E, \theta = 0) \).

We have assumed an isotropic absorption coefficient through the second of the points above though this may not be the case for highly strained wells [7]. The last assumption is made because, even at 1000 suns, the highest angle of incidence will be \( \theta \approx 2^\circ \) which will have little impact on the photocurrent.

With the above conditions and accounting for all possible optical paths [5, 7], the angular part of equation (2) reduces to summing over the paths shown in Figure 2.

Figure 2. The light paths contributing to absorption in a cell. Blue is the active region and red is the substrate. The light paths above are described quantitatively by:

\[ \int \int \int dS \int d\Omega \int dE \alpha(E, \theta) d\Omega dS = \]
\[ 2\pi \int \int \int [1 - r(1 - e^{-r}) \cos \theta d(\cos \theta)] d\theta d\phi \]
\[ +2\pi \int \int \int [1 + r e^{-r}(1 - e^{-r}) \cos \theta d(\cos \theta)] d\theta d\phi \]
\[ +2\pi \int \int (1 - e^{-2r}) \cos \theta d(\cos \theta) \]

Where \( \theta_d = \sin^{-1}(1/n) \) is the critical angle and \( r = \alpha d/\cos \theta \).

Detailed balance is particularly applicable to high concentration conditions where radiative losses become important relative to non radiative processes.

All following results are calculated under 500 suns of AM1.5d low AOD.

3 BULK CELLS

The simplest application of the method described above is to a single junction cell comprised of material of a single band-gap. In Figure 3 we show the effect on such a cell of varying the strength and edge of its absorption. In this case, decreasing absorption only significantly affects efficiency and not the optimum bandgap. This is the case for all absorptivities, though Figure 3 encompasses a smaller region of practical interest for clarity.

Figure 3. Efficiency limits of bulk cells at 500 suns concentration AM1.5d low AOD with variable band-edge and absorptivity.

4 SINGLE JUNCTION QWSCS

In the case of a single junction quantum well solar cell we model the quantum efficiency with a square absorption profile as shown in Figure 4. The bulk band edge is fixed at that of GaAs (873nm) and we assume that all incident photons with wavelengths below this value are absorbed.

Figure 4. The absorptivity profile used to model single junction QWSCs.

The absorption profile above leads to Figure 5 which plots the absorptivity of the quantum wells against their band edge at 500 suns in a low-AOD spectrum. The dotted line shows the iso-efficiency contour above which a quantum well solar cell is advantageous with respect to a control bulk GaAs cell. The graph implies that shallow quantum wells enhance efficiency in the radiative limit though it may be that this effect would be less pronounced in the case of a smoother bulk band edge. This result is in agreement with Figure 3 for unity QW absorptivity. Note that 1100nm only represents the global optimum band-edge for quantum well absorptivities above around 0.9. Shallow, single junction QWSCs outperform deep well cells under all realistic absorptivities in the radiative limit providing we ignore the effects of directional emission [7] and/or hot carriers. Both of these effects should be more pronounced in deep well cells.
5 EXCITONS

Quantum confinement in quantum well solar cells leads to an exciton peak at the QW band edge which will simultaneously enhance the photo current and the radiative dark current. If we can determine which of these two effects will dominate the performance of the cell it may be possible to engineer their shape and strength in order to enhance efficiency. We model exciton absorption with a Gaussian curve as in and then adjust the width and height within empirically realistic bounds. The results in Figure 6 reveals that in the case of shallow well cells, reduced excitonic width is the best path to efficiency enhancement given that at present, a typical cell has coordinates of approximately (5,1.5).

6 TANDEM QUANTUM WELL SOLAR CELLS

Quantum wells are well suited for use in tandem cells since the GaInP and GaAs bandgaps used in conventional two- and three-junction solar cells are both higher in energy than the optimum configuration. Varying both quantum well absorptivities in unison with one another enables us to locate the optimum band-edge configuration of the quantum wells at a specific absorptivity. Despite this, up to now QWs have not been incorporated into an InGaP top cell. We have recently achieved this and the response of this cell is shown below.
Figure 9 illustrates the effect of radiative coupling on the robustness of a slightly bottom cell limited tandem to variations in spectral content in agreement with previous literature for bulk cells [8].

We are able to deduce the behaviour of the ideal band-edge combination and efficiency with respect to varying absorptivities.

![Figure 10. Optimum tandem cell band-edges as a function of QW Absorptivity. The bulk band edges used were 660nm and 873nm.](image)

Figure 10. Optimum tandem cell band-edges as a function of QW Absorptivity. The bulk band edges used were 660nm and 873nm.

Bottom cell QWs are advantageous for low absorptivities because the bulk tandem with unity absorption is current limited by the bottom cell. Nevertheless, it is clear that QWs in the top cell are also beneficial once the QEs of the QWs rise to around 50%. The discontinuities in the optimum band edges arise when one local peak in band edge space rises above the global peak causing the optimum to shift instantaneously. Each of these events corresponds to a new gradient of efficiency against absorptivity.

7 CONCLUSIONS

We have described a technique to predict detailed balance efficiency limits without the assumption of unity quantum efficiency. The ideal band edge for a bulk, single junction cell for all levels of quantum efficiency lies near 1100nm. For all presently realisable QWSCs however, it is about 925nm. Tandem cells benefit from QWs in the bottom cell for low QW QEs but top cell QWs are only advantageous within the model for QW QEs above around 50%. Radiative coupling in tandem QWSCs has the potential to significantly decrease spectral sensitivity and enhance the performance of bottom cell limited tandems.

8 REFERENCES


