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# Quantum Well Solar Cells

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This paper reviews the experimental and theoretical studies of quantum well solar cells with an aim of providing the background to the more detailed papers on this subject in these proceedings. It discusses the way quantum wells enhance efficiency in real, lattice matched material systems and fundamental studies of radiative recombination relevant to the question of whether such enhancements are possible in ideal cells. A number of theoretical models for QWSCs are briefly reviewed and more detail is given of our own group's model of the dark-currents. The temperature and field dependence of QWSCs are all briefly reviewed.

## 1. Introduction

This paper will review the development over the past decade of the quantum well solar cell (QWSC). The study of quantum wells (QW) and, more recently, quantum dots (QD) have dominated opto-electronic research and development for the past two decades. QWs have been very extensively studied in reverse bias where they are used in photodetectors and optical modulators. In forward bias at forward current, QWs are already employed in lasers and LEDs. However, for forward bias and reverse current, the quadrant of the IV plot where photovoltaic (PV) power can be extracted, QWs have been much less extensively studied. The physics of this quadrant is, however, interesting in itself as well as having important potential applications in PV. The people who have worked in this area could be assembled in one room. In fact many of them were at the workshop and their work is represented in these proceedings.

The Quantum Photovoltaic (QPV) group at Imperial College has pioneered this area. I will be concentrating on their work as I know it best. I will try to give due credit to others who have contributed, particularly those present at the meeting! I apologise in advance that I will not have the space to do justice to everyone's work.

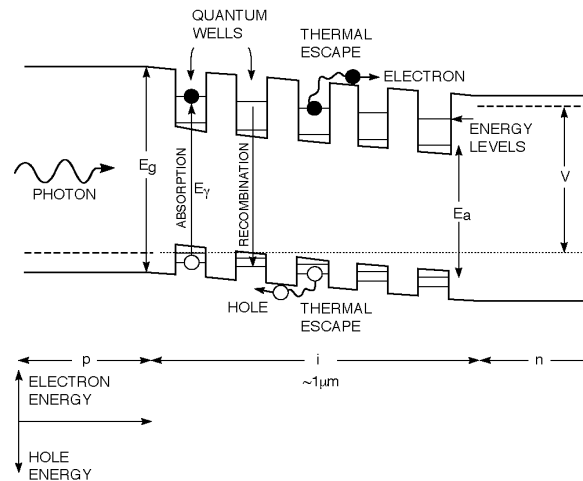
In this review I will introduce the advantages of QWs for solar cells and discuss some of the fundamental aspects that have caused some controversy. I will discuss work by ourselves

and other authors on modelling dark-currents and results on the temperature, radiation and field dependence of QWSCs.

I will not have space to cover three important areas of our current work. The use of strain-balanced quantum wells for tandem and thermophotovoltaic (TPV) applications are discussed by Ned Ekins-Daukes [1] and Carsten Rohr [2], respectively, in other papers in these proceedings. Details of our novel use of quantum dots, as the replacement for the dyes in a luminescent concentrator, can be found in Ref. 3.

## 2. Quantum Well Solar Cells

Fig. 1 shows a schematic of a QWSC. An intrinsic region is inserted into a conventional p-n solar cell to extend the field-bearing region. The importance of maintaining the built-in field across the i-region will be discussed in Sec. 5. The quantum wells (QWs) extend the absorption below the bulk band-gap  $E_g$  to threshold  $E_a$ . If the field is maintained across the i-region, the carriers produced by the extra photons absorbed in the well escape to the bulk cell and contribute extra current with high quantum efficiency (QE) at room temperature [4]. There is some voltage loss to which we will discuss. However, we have demonstrated, in three lattice-matched QW material systems, that the current enhancement of the QWs is sufficient to overcome the voltage loss. Hence, in lattice-matched systems, the wells can enhance efficiency compared with conventional cells with the bulk- band-gap  $E_g$ .

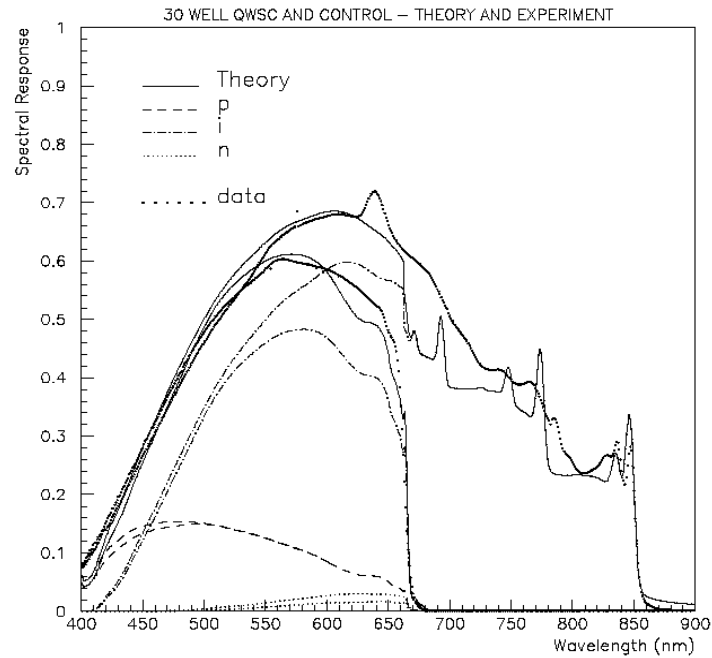


**Fig. 1.** Schematic energy band diagram of a quantum well solar cell.

The extra current comes for the extended absorption at longer wavelengths and also from the increased absorption in the i-region above the quantum well. This can be seen in Fig. 2 where the spectral response (SR-quantum efficiency at zero bias) is shown for a 30 QW AlGaAs/GaAs QWSC and a homostructure AlGaAs control made entirely with the barrier material of the QWSC. The i-region has the same thickness in both cells. We have developed a programme SOL which can fit the SR of QWSC and control cells in a number of III-V systems [5, 6].

The question of what output voltage the QWSC will achieve in the ideal limit has been a matter of some controversy as will be discussed in Sec. 3. However, we have demonstrated in three lattice-matched multi-quantum well (MQW) systems that the open-circuit voltage of the QWSC is greater than the control sample made from *well material* [7]. The enhancement is greater than that expected from the increase in absorption threshold  $E_a$  due to the effect of

quantum confinement. The effect results from the dark-current being *lower* than expected for bulk cells at comparable  $E_g$  [7]. This will be discussed further in Sec. 3 & 4.



**Fig. 2.** Spectral response (heavy dots) for a 30-well AlGaAs/GaAs QWSC and a homostructure AlGaAs control cell. The i-region has the same thickness in both cases. Thin lines are fits with the programme SOL.

### 3. Fundamental Efficiency Limits

It was relatively straightforward to show that QWs enhance solar cell current, but some authors claim [8] that, in the radiative limit, the voltage would be determined by the lowest band-gap in the system ( $E_a$ ). Fundamentally, the output voltage is determined by the variations in the quasi-Fermi levels for the electrons and holes across the cell. However, the way these behave in a QW system was not known. In 1994 Antonio Marti and co-workers produced a detailed balance model for quantum well cells which assumed that [8]:

- 1) Cells are in the ideal limit when all recombination is radiative.
- 2) Absorption is 100% for photon energies greater than the effective band-gap  $E_a$ .
- 3) In the ideal situation the quasi-Fermi level separation ( $\lambda E_F$ ) is equal to the applied bias at all points.

Under these assumptions situation an ideal QWSC cannot have higher efficiency than the conventional homostructure cell with the band-gap corresponding to maximum efficiency.

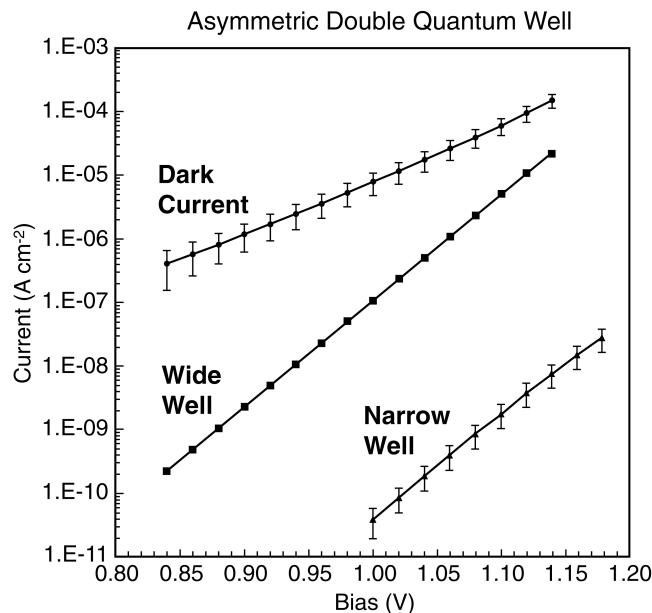
In order to investigate if this model holds, we have developed a method for determining the quasi-Fermi level separations [9,10] that we have demonstrated on single (SQW) and asymmetric double (DQW) quantum well samples [10,11]. The method involves studying radiative recombination by extracting the electroluminescence (EL) signal at room temperature in absolute units. The EL is calibrated by comparison with the photoluminescence (PL) signal when illuminating in the QW with a certain generation rate  $G$ . The PL is calibrated by comparing the forward bias PL signal with reverse bias photo-conductivity (PC) at low temperatures (e.g. 40 K) where non-radiative recombination is small. In this case the large field across the well in reverse bias will extract all the carriers. In *reverse bias* therefore, the PC measures the rate of carrier escape from the well and hence the generation rate  $G$ . In *forward*

*bias* at low temperatures all the carriers recombine to give the PL signal. Hence the maximum integrated luminescence rate is equal to  $G$  and the device is calibrated for all further luminescence by that sample.

We use a generalised, detailed balance approach to fit the absolute EL spectrum  $L(E,F)dE$  as a function of photon energy and field  $F$  in the wells as below

$$L(E,F)dE \ll \frac{2n^2L_w}{h^3c^2} \frac{\kappa(E,F)E^2}{e^{(E-\lambda E_F)/k_B T} - 1} dE$$

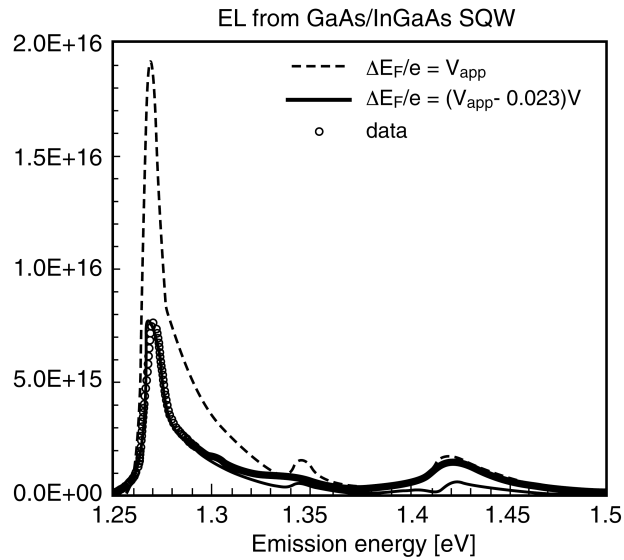
The fit is made in terms of  $\lambda E_F$  and the absorption coefficient  $\kappa(E,F)$ , which we calculate from first principles [9,10] using the same approach as in the programme SOL which fits the SR of the QWs. Confidence in our method is provided by the voltage dependence of the integrated radiative currents which we extract. These should have unit ideality factor if they result from radiative recombination. In Fig. 3 we show room temperature results for our AlGaAs/GaAs asymmetric DQW samples [11]. We have also managed to extract the much smaller radiative signal from the narrower of the two wells. Both radiative components have slopes consistent with unit ideality factor over a large number of decades. In contrast, the dark-currents of the cells, dominated by non-radiative recombination, have ideality near 2.



**Fig. 3.** Radiative currents extracted from the wide and narrow wells of double quantum well devices compared with the dark currents of the devices.

We have shown that, at room temperature in SQW samples and the dominant wider well of DQW samples, the quasi-Fermi level separation ( $\lambda E_F$ ) is less than the applied bias i.e. recombination is less than predicted on the assumptions of the detailed balance arguments in Ref. 8.

In the case of GaAs/InGaAs SQW samples we have been able to observe the radiative recombination signal from the bulk GaAs in addition to the SQW [10].



**Fig. 4.** Calibrated EL from a GaAs/InGaAs SQW device at room temperature. The signal at 1.42 eV from the barrier can be modelled with  $\lambda E_F$  equal to the bias ( $V_{app}$ ). The well signal requires a reduced  $\lambda E_F$ .

As shown in Fig. 4, we can fit the bulk GaAs-cell signal assuming that the quasi-Fermi level separation is equal to the bias. However, the well signal, in the same sample, can only be fitted if the quasi-Fermi level (and hence the radiative recombination) is reduced significantly.

Our DQW results show that the quasi-Fermi level separation is different in wide and narrow wells. The temperature dependence suggests that the quasi-Fermi level of the wide-well approaches the bias as the temperature is reduced and carrier escape becomes less likely [11]. This observation adds strength to our conjecture that the reduced radiative recombination in the QW results from the escape of the carriers from the well to the wider band-gap region at room temperature.

These results clearly demonstrate that radiative recombination in QW systems cannot be described by the assumption that the chemical potential is equal to the bias. Martin Green pointed out that that a feature of “Third Generation” cells is that the chemical potential is not equal to the bias [12]. We therefore believe that our results clearly demonstrate that the QWSC is a “Third Generation” device.

The observation that if the QW and barrier are radiatively coupled then the system should be described by more than one quasi-Fermi level was first made by Stefan Ketteman and Jean-Francois Guillimoles [13]. This idea has been taken further recently by Stephen Bremner, Richard Corkish and Christiana Honsberg [14]. They have modelled the situation represented in Fig. 5. The transitions they assume to be radiative are indicated by arrows. They conclude that, in the radiative recombination limit, if the well to barrier transition is also radiatively coupled, quantum well cells are capable of achieving 63.2% efficiency. Further details of this model are given in the paper of Christiana Honsberg [15].

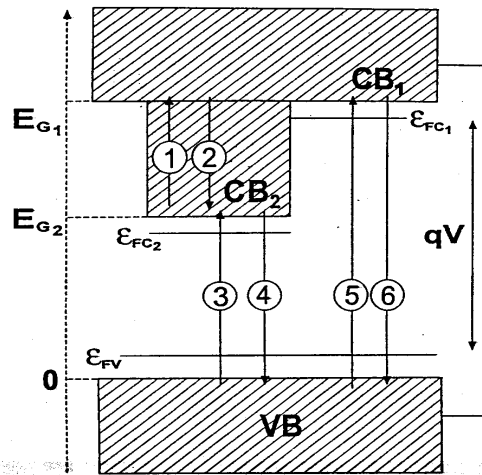


Fig. 5. Schematic representation of the radiative transitions in the model of Ref. 14.

#### 4. Modelling Quantum Well Solar Cells

A little before the detailed-balance model of Ref. 8 appeared, Richard Corkish and Martin Green modelled MQW cells by introducing the idea that the QW contribution could be added as an incremental cell in parallel with a host homostructure cell corresponding to the barrier [16]. In contrast with the model of Ref. 8, their model predicts a small amount of efficiency enhancement for small well widths in the ideal limit.

The next model, due to Mohaidat et al., involved a detailed calculation of the resonant tunnelling contribution to electron transport in MQW systems [17]. Their calculations emphasised that carrier escape would be enhanced compared to recombination if the resonant tunnelling condition was optimised. This model has been tested in a series of measurements on GaInAsP/InP based systems [18]. This data is discussed further in Sec. 5.

Neal Anderson modelled the QWSC as a baseline, realistic p-n junction with an ideal i-region and MQW [19]. This model was successful in reproducing the  $V_{oc}$  performance of some InGaAs/InP QWSCs and their controls [20]. Neal has gone further in comparing differing QWSC models in his review paper in these proceedings [21].

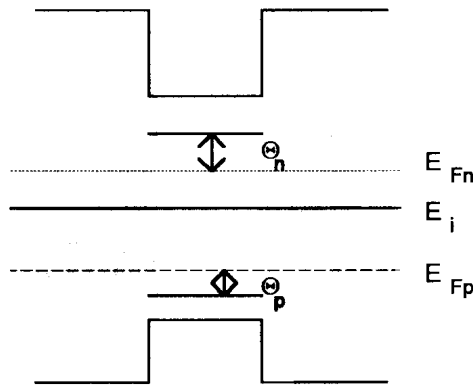
The model of Argyrios Varonides [22] is notable for its comprehensive treatment of the tunnelling and thermionic emission contributions to carrier collection. This model has recently been compared with experimental data, on the temperature dependence of AlGaAs/GaAs QWSCs as will be discussed in the next section. He has also developed his model further as discussed in his own paper [23].

Apart from the extension of our spectral response fitting programme, discussed in Sec. 2, to different materials, our main modelling effort at Imperial College has been in the fundamental studies (Sec. 4), and attempting to explain experimental data on the dark-current behaviour of QWSCs [24, 25]. As in the case of the PL and EL studies discussed in Sec. 4, we have built on the success of SOL. This means that we are able to calculate from our knowledge of the electron and hole eigenstates in the QW the density of states of the carriers as a function of energy and field. Because of differences in effective mass, the conduction and valence band density of states differ, and this asymmetry changes as one moves from barrier to well. Given that in equilibrium the Fermi-level  $E_F$  is constant across interface, the intrinsic Fermi energy level  $E_i$  must be discontinuous between well and barrier. We therefore introduce shifts in the intrinsic

level  $E_{Fn}$ ,  $E_{Fp}$ , defined as in Fig. 6, which can be calculated from the QW eigenstate energies. It should be noted that the  $E_{Fn}$ ,  $E_{Fp}$  parameters depend in a known way on the QW parameters. The electron density in the well are then related to the quasi-Fermi levels by:

$$n \ll n_i e^{(E_{Fn} - E_i) / k_B T}$$

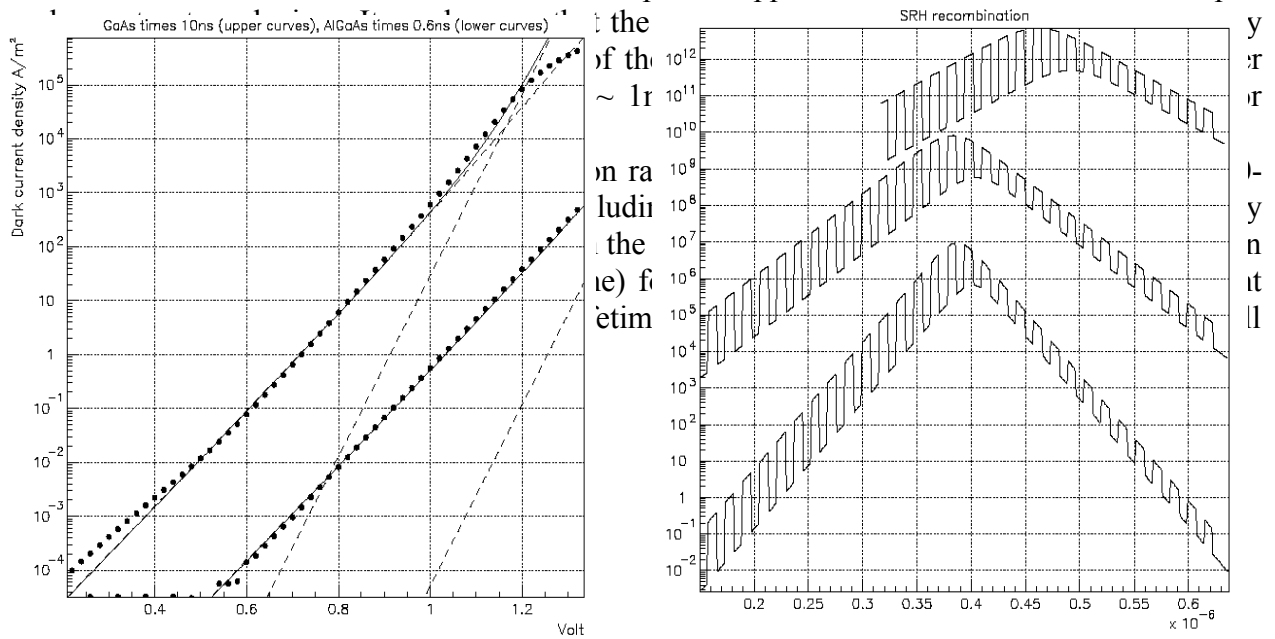
A similar expression holds for the hole density.



**Fig. 6.** Definition of the parameters  $\phi_n$ ,  $\phi_p$  which shift the intrinsic Fermi energy between barrier and well.

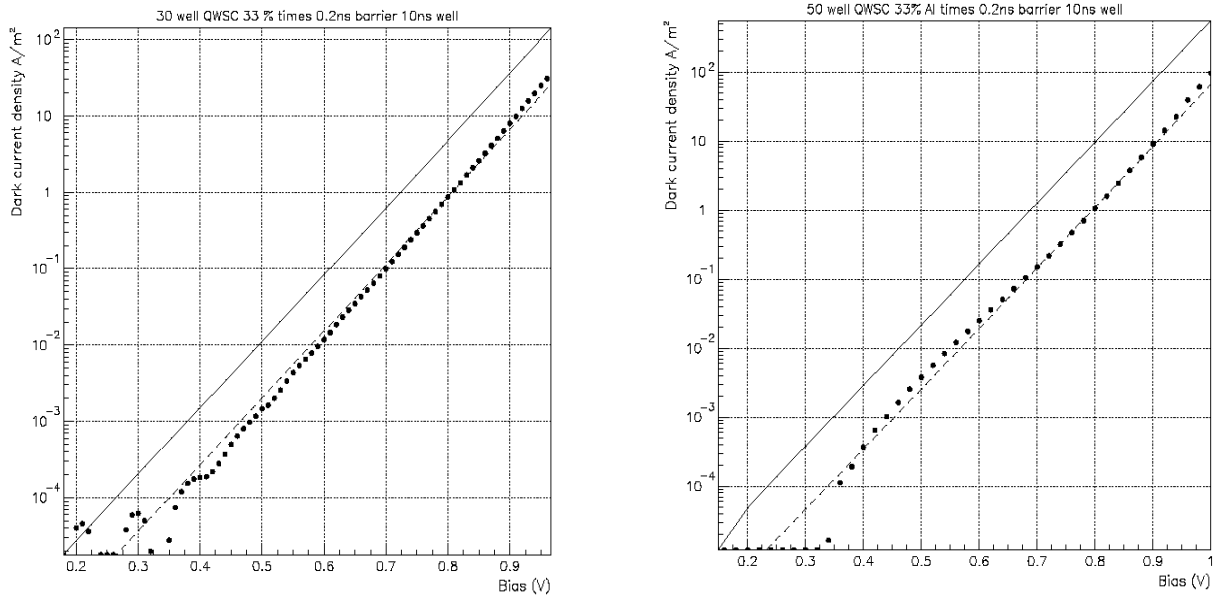
We have investigated two approaches to solving for the  $n(x)$  and  $p(x)$  variation throughout the i-region, either assuming the *depletion approximation* or a fully *self-consistent calculation* including the constraints of Poisson's equation. We have shown that the two approaches are equivalent at least up to voltages of the order of  $V_{oc}$ . Once we have the carrier densities then we can calculate a recombination rate assuming the Shockley-Hall-Read approach, as long as we can estimate the recombination lifetimes, which depend on material quality. We find the results are not particularly sensitive to differences between the electron and hole carrier lifetimes, so we can equate them and are left with two material quality parameters to determine, the carrier lifetime in the barrier and the well,  $\tau_B$  and  $\tau_W$  respectively.

We determine these two parameters by fitting homostructure or double heterostructure controls which have i-regions formed from the material of the barrier or the well respectively. The procedure can be illustrated by considering the example of the AlGaAs/GaAs system. Fig. 7a shows the fits made with this model in the depletion approximation to GaAs and AlGaAs p-i-

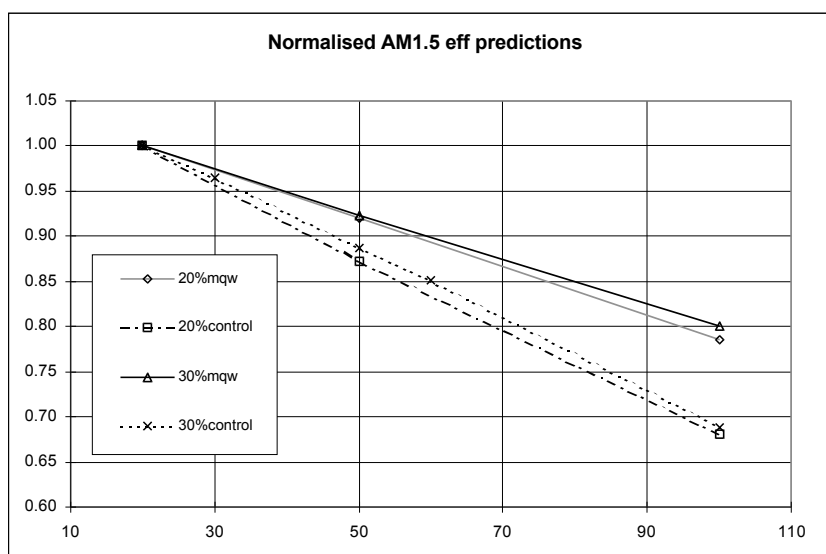


**Fig. 7.** a) Fits with model described to AlGaAs and GaAs heterostructure p-i-n controls.  
 b) Recombination as a function of position in i-region for 30 MQW cell.

In both cases the predictions using the lifetimes determined from the homostructure controls falls significantly above the experiment. Agreement with the data can be achieved (as in the dashed lines in Fig. 8) if one assumes that, as we have demonstrated in the SQW and DQW devices (see Sec. 3), the quasi-Fermi level separation is reduced in the wells compared to the barrier. Our fits to double-heterostructures and MQWs in the GaInAsP/InP system show a similar effect.



**Fig. 8.** Experimental dark currents (heavy dots) for AlGaAs/GaAs QWSCs with a) 30 wells and b) 50 wells compared with model using homostructure control lifetimes (light dots) and with reduced  $\lambda E_F$  (broken lines). These results give further support to our view that recombination in quantum wells is reduced compared to that in homostructures. However, we still need to understand why the quasi-Fermi level reductions in MQWs, which we observe in this way, are considerably larger than we observe in the radiative signal in SQW and DQWs.



**Fig. 9.** Normalised efficiency of 30 well  $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$  MQWs (Al fraction  $x = 0.2$  and  $0.3$ ) measured in a 3000K blackbody spectrum and corrected using QE measured as a function of temperature to AM1.5 conditions. Comparison is with control, homostructure  $\text{AlGaAs}$  p-i-n cells with comparable  $x$  values.

## 5. Temperature, Radiation and Field Dependence

We have demonstrated that  $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$  MQW cells have better T-dependence of efficiency than comparable control heterostructure cells made from the barrier materials ( $\text{Al}_x\text{Ga}_{1-x}\text{As}$  with Al fraction  $x = 0.2$  and  $x = 0.3$ ) as shown in Fig. 9 [26]. The Al = 0.3 MQW cell also has better temperature coefficient of efficiency than a control cell made from the well material (GaAs).

The improved efficiency does not come from an increase in the level of the spectral response. This is consistent with the observation in Sec. 2 that the QE for carrier escape from the wells saturates at a value close to unity at room temperature. The improvement in efficiency appears to come from a relative improvement in the dark-current with increasing temperature.

Improved temperature dependence of  $\text{AlGaAs}/\text{GaAs}$  QWSCs has also been seen by Aperathitis et al. [27]. The data have been explained by the model of Varonides discussed in Sec. 4 in terms of differing contributions from thermionic and tunnelling currents [28].

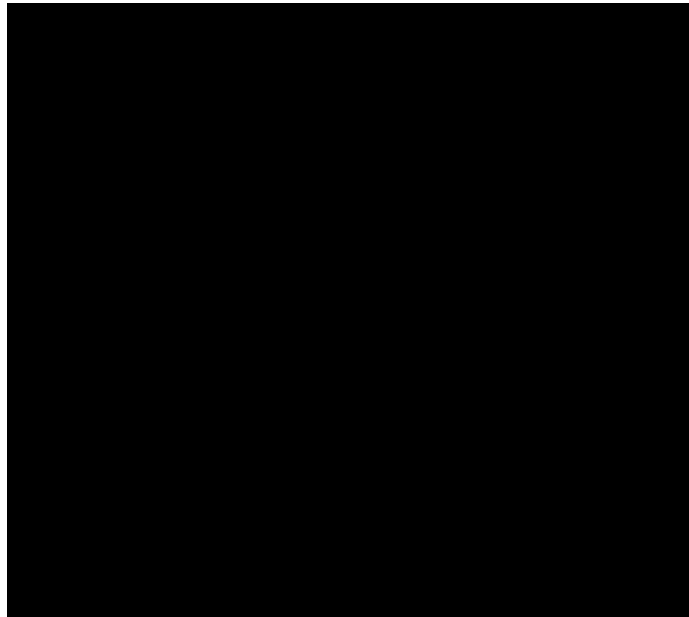
Evidence that  $\text{InP}/\text{InAsP}$  strained MQW cells demonstrate an improved radiation tolerance compared to homostructure controls is discussed by Alex Freundlich in another paper at this meeting [28]. The most likely reason for the improved performance is that in a MQW cell a large proportion of the carrier collection occurs in the i-region where the collection is by drift rather than in the base where collection is by diffusion.

The importance of the built-in field to the operation of QWSC is the final topic to be reviewed in this section. The first report of efficiency enhancement in QWSCs showed that background doping must be low to preserve field across i-region and keep the QE and collection efficiency high [4]. The importance of a critical built-in field has also been demonstrated in strained  $\text{InAsP}/\text{InP}$  QWSCs [29]. Our extensive studies of carrier escape from SQW and DQWs show that the holes dominate with the mechanism being thermally assisted tunnelling which is strongly field dependent [30]. Studies of the temperature and bias dependence of photoluminescence in addition to photoconductivity, show that the electron and hole escape is linked by the influence of space-charge on the field [31]. Similarly, the photoluminescence signal from  $\text{GaInAsP}/\text{InP}$  QWSCs shows field screening [32]. The latter group has recently demonstrated sequential resonant tunnelling effects in QWSCs at critical field values [33]. In the

original proposal for the QWSC [34] it was pointed out that resonant tunnelling might reduce recombination effects and that variable well-widths could enhance this. The authors of Ref. 33 have demonstrated a sequential tunnelling enhancement in the bias dependence of the dark-current and photocurrent in a GaInAsP/InP QWSC with 16 equally spaced wells. Most interestingly, in view of the discussion in Sec. 3, they observed a that the photoluminescence signal was reduced at the resonant bias which they interpreted as a reduction in the radiative recombination rate at the resonant field.

Some unpublished work of our group is relevant to question of field dependence [34]. We have had a sample grown with 14 strained InGaAs/GaAs QWs in the neutral n-region of a p-n cell. The measured spectral response of this cell is compared in Fig. 10 with a similar cell with 15 strained InGaAs QWs in the i-region and with the comparable p-n homostucture control cell. One sees that the quantum wells in the n-region contribute about one fifth as strongly as the i-region wells, i.e. only approximately 3 wells are contributing to the absorption. Confirmatory information comes from the QE just above the bulk GaAs band-gap. The main contribution to absorption here is the n-region base layer, which has a considerably reduced QE. Our spectral response fitting programme suggests this reduction results from a reduction of the hole minority carrier diffusion length due to the presence of the wells in the n-region to around 2 barrier widths. This is therefore consistent with saying that only the three wells within a (reduced) minority carrier diffusion length contribute carries that are collected by the built-in field.

This is a warning for those designing quantum dot solar cells which rely on diffusion alone, without drift.



**Fig. 10.** Spectral response of a strained InGaAs/GaAs p-n MQW device with the 14 wells in the neutral n-region compared with its p-n control and a p-i-n cell with 15 wells in the i-region.

From this last discussion we can see that there are problems with incorporating wells and quantum dots in field free regions. We have also looked at the performance of self-assembled quantum dots in a p-n structure and found their absorption to be rather low and the non-radiative recombination very high. As an alternative, we are studying what quantum dots can contribute to one old, but potentially very useful idea, the luminescent (or fluorescent) concentrator. This idea originally proposed in Ref. 36, is discussed in Ref. 3.

## 5. Conclusions

The efforts of a number of researchers, from our own and other groups, have clearly demonstrated that quantum wells enhance current and efficiency relative to conventional cells with the barrier band-gap in lattice matched systems. They also enhance voltage compared to conventional cells with the well band-gap. QWSCs have advantages in terms of temperature dependence of efficiency, which is important in concentrator and TPV applications, and in radiation tolerance.

Our own studies of the radiative recombination contribution to the dark-current have shown that single and double QW systems in a built-in field have reduced radiative recombination and have quasi-Fermi level separation which is less than the external bias. These results demonstrate that quantum well cells can already claim to belong to the “Third Generation” of solar cells in Martin Green’s definition.

All our experiments on  $\lambda E_F$  have been conducted on the dark-current. We appreciate that these should be extended to light bias conditions where the results might well be different but the experiments are not simple. An extension of this type of experiment would look for direct evidence for photonic coupling between well and barrier to test the Bremner, Corkish and Honsberg model. We also need to extend these studies from SQW and DQW cells to MQWs. Here the experimental problem is that we cannot use the calibration method described in Sec. 3 as it is not possible to turn off the photo-current at low temperature. Carrier escape in MQWs is too efficient.

On the theoretical side, our own dark-current modeling of practical MQW cells supports the observation of reduced  $\lambda E_F$  in the wells but more work is required to understand why the suppression appears to be larger in these non-radiative currents than in the radiative currents of SQWs and DQWs. There is a difficulty in extending this model to the interesting situation of the strain-balanced QWSCs as in this case it is not possible to determine the carrier lifetimes which depend on material quality as there are no appropriate bulk homostructures or heterostructures. It is the great advantage of the strain-balanced QWSC that it can produce effective band-gaps that cannot be achieved in bulk material.

For the reasons discussed in Sec. 5 we believe that the built-in field is important for the operation of the QWSC. We believe that the theories for the limiting efficiency should be modified to incorporate the effects of the field. This could be the key to understanding the quasi-Fermi level variation. The experimental studies of radiative recombination in MQW systems will also require a treatment of photon recycling effects.

There is still much to be done for a full understanding of this Third Generation PV cell, particularly in the radiative limit. However, this will not inhibit the development of the applications discussed in Refs. 1 and 2. These deal with practical, non-radiative-dominated material. It could turn out that the most important property of the QWSC is the variety of band-gaps that can be achieved with the strain-balanced version.

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