

# Quantum wells for high efficiency photovoltaics

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## ABSTRACT

Over the last couple of decades, there has been an intense research on strain balanced semiconductor quantum wells (QW) to increase the efficiency of multi-junction solar (MJ) solar cells grown monolithically on germanium. So far, the most successful application of QWs have required just to tailor a few tens of nanometers the absorption edge of a given subcell in order to reach the optimum spectral position. However, the demand for higher efficiency devices requiring 3, 4 or more junctions, represents a major difference in the challenges QWs must face: tailoring the absorption edge of a host material is not enough, but a complete new device, absorbing light in a different spectral region, must be designed. Among the most important issues to solve is the need for an optically thick structure to absorb enough light while keeping excellent carrier extraction using highly strained materials. Improvement of the growth techniques, smarter device designs - involving superlattices and shifted QWs, for example - or the use of quantum wires rather than QWs, have proven to be very effective steps towards high efficient MJ solar cells based on nanostructures in the last couple of years. But more is to be done to reach the target performances. This work discusses all these challenges, the limitations they represent and the different approaches that are being used to overcome them.

**Keywords:** quantum wells, III-V solar cells, concentrated photovoltaics

## 1. INTRODUCTION

### 1.1 Historic perspective

Over the last few years, the research in strained-balanced multi-quantum well (MQW) structures for photovoltaics (PV) has been very active. The most successful application of this technique was a GaAs, single junction device with multiple InGaAs/GaAsP quantum wells, that had an efficiency of 28.3% under AM1.5D 416 X, breaking a 20-year long world record for single junction devices<sup>1</sup>. More recent research in this field has already produced dual-junction devices with efficiencies close to their bulk counterparts (30.6% compared to 31.7%). Moreover, in 2012 JDSU reported the fabrication of triple junction (3J) devices with MQWs in two of the junctions and with a maximum efficiency of 42.5% under concentration<sup>2</sup>, close to the 44.4% world record at that time<sup>3</sup>.

But why this interest for QWs in PV? What are they and what can they offer?

In order to reach the maximum conversion efficiency, MJ solar cells – that in the most common configuration are made of several solar cells connected in series by means of tunnel diodes – need a specific combination of bandgaps in each subcell, so that they all produce the same current and where the voltages of the cells are added. Theoretical calculation of the ideal bandgap combination is relatively simple but real semiconductor materials that could reproduce those conditions are not easy to find. First MJ solar cells in the 70's were made of AlGaAs/GaAs and latter designs greatly improving the efficiency were developed with GaInP/GaAs in the late 80's<sup>4</sup>. Neither of them were optimal designs in terms of absorption edges: the bandgap of both subcells should be lower.

The problem arose mainly with the GaAs subcell: at the time of developing the first MJ solar cells, there was no material with lower bandgap that could be fabricated with the same lattice constant and good quality. As with most semiconductor devices, low defect density was essential in efficient solar cells. A bottom junction made of germanium would finally be introduced in the mid-late 90's, producing the most common design that dominates the market of MJ solar cells, still nowadays: the triple junction made of GaInP/Ga(In)As/Ge solar cell (Figure 1, left). But despite this improvement, the design was far away from the optimal combination of bandgaps. Other approaches such as metamorphic growth (upright or inverted)<sup>5</sup>, wafer bonding<sup>6</sup> or the use of mismatched alloys (dilute nitrides, in particular)<sup>7</sup>, have been developed in recent years to tackle the lack of lower bandgap materials compatible with the

growth on GaAs or Ge (figure 1, center). They have achieved very high efficiencies at laboratory level but at the cost of a more complex or lengthy fabrication process, raising questions about its viability at the industrial level.

While QW had been known for a long time, their application as light absorbers in solar cells dates only back to the early 90's<sup>8</sup>. The driven force behind that initial research was precisely the possibility of tuning the bandgap of a solar cell to better match the ideal absorption edges in the newly developed and very promising, but suboptimal, MJ solar cells. Further development of the technology along that decade lead to the first designs of strain balanced quantum wells, which allowed for a breakthrough in the QW-based solar cell designs<sup>9</sup>. This strained quantum well structures hold several advantages, including a defect-free crystal structure, a relatively straight forward growth process or the possibility of adjusting the absorption edge as a function of the particular solar spectrum of a given region.

Despite their potential and demonstrated performance back in 2013<sup>2</sup>, further development as a world record, industry compatible product have been hindered by several factors, being the main one their limited absorption compared to bulk materials.

In this work, we first summarize the main properties of QWs, focusing on strain balanced MQW structures, and the characteristics that are essential for their application in a solar cell. Then, we explore the different aspects of the design of a QW solar cell that can contribute to boost its performance. Finally, we will discuss the target properties that a QW-based solar cell must fulfil in order achieve the highest efficiencies, comparing those targets with the current status of the technology.

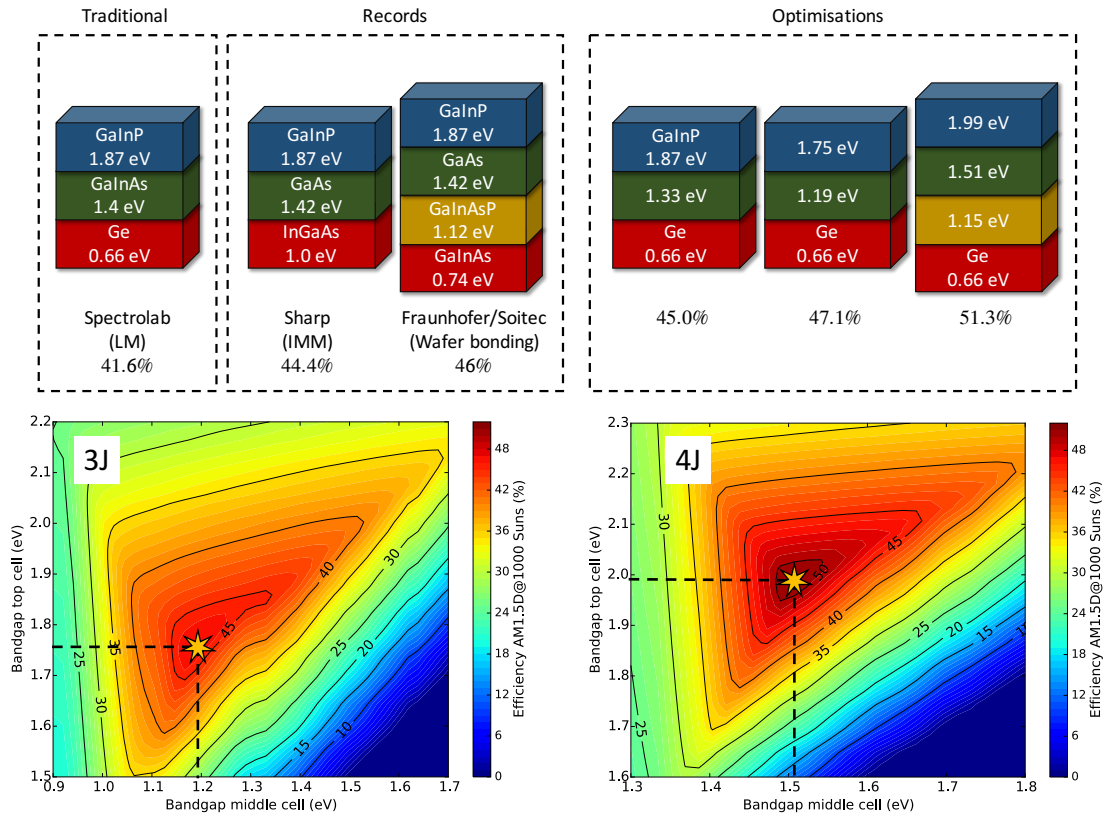


Figure 1: From left to right: traditional 3J solar cell and world record 3J and 4J solar cells<sup>5,6,10</sup>. LM and IMM stand for lattice matched and Inverted metamorphic, respectively. On the right, three optimizations done to the middle, the top and the upper-middle cells in order to achieve the maximum efficiencies under a the AM1.5D solar spectrum at 1000 suns. In the 4J design, the lower-middle cell bandgap has been fixed to 1.15 eV. Bottom: Efficiency maps for the 3J and 4J designs. The stars indicate the optimal structures shown above. Values calculated according to reference [11,12].

## 1.2 Simulation and modelling

Along this work we present numerical calculations of the performance of MJ solar cells as a function of the bandgap of the constituent subcells, as well as of QW-based devices.

For the calculation of the properties of QWs and QW-based solar cells we have used Solcore. This is a powerful multi-tier modelling framework for simulation of nano-structured solar cells written in Python and Fortran and developed at Imperial College London<sup>13,14</sup>. Some of their features are a 1D arbitrary potential Schrödinger equation solver and absorption calculator, k-p band structure solver, spectral irradiance model and database, a multi-junction quantum efficiency and IV calculators and a coupled drift-diffusion Poisson solver. The last feature allows calculating realistic transport of carriers across the cell, recombination profiles, charge accumulation and screening effects<sup>15</sup>.

The efficiency calculations of MJ devices included in Solcore, such as those presented in Figure 1, have been done following a similar method to that described in references [11] or [12]. A square external quantum efficiency of 90% is assumed in all cases, consequence of the antireflection coating and the shadowing losses related with the top metal grid. Radiative efficiency – in the sense described in [11] – is set to 30% except for the Ge junction where 1% is used instead accounting for its indirect bandgap nature. A series resistance of 12 mΩ/cm<sup>2</sup> is added to the calculations in order to provide realistic efficiency values at high irradiance levels. Radiative coupling between subcells is neglected in the calculations.

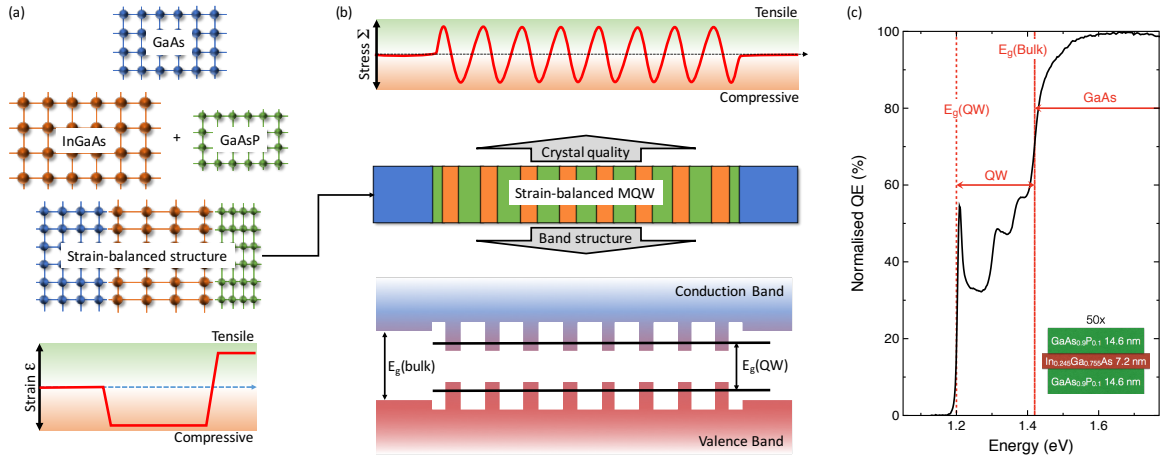


Figure 2: (a) A strain balanced structure can be achieved by combining materials that have strain with opposite sign when grown pseudomorphically on a given substrate. In this example, InGaAs and GaAsP adapt their in-plane lattice parameter to fit that of GaAs. (b) When correctly design, a strain-balance structure allows the grow of many alternating compressive/tensile layers, such as MQWs (center). Overall, the accumulated stress of the structure must be zero in order to avoid defects (top). The resulting structure is a metamaterial with an effective bandgap, defined by the confined states of the QWs, lower than that of the bulk (bottom). (c) Such solar cell can absorb lower energy photons and therefore be better suited for an optimum MJ solar cell.

## 1.3 Growth of multiple QW structures: strain-balance technique

Quantum wells are thin slabs (~nm) of a lower bandgap semiconductor surrounded by another one with higher bandgap. Typical examples are GaAs QWs with AlGaAs barriers grown lattice matched to GaAs, InGaAs/GaAsP also on GaAs or InGaAsP/InGaAsP on InP. The difference in bandgap between well and barrier, and the resulting confinement of carriers leads to a modification of the band structure of the material – the quantization of the energy levels inside the well – that can be exploited in optoelectronic applications, such as in lasers<sup>16</sup> or infrared photodetectors. For tailoring the absorption edge of MJ solar cells, the most common type of QWs are made of InGaAs/GaAsP, able of absorbing sunlight with energy lower than GaAs and targeting the ideal absorption edges of 1.18 eV or 1.15 eV shown in Figure 1.

InGaAs has a larger lattice parameter than GaAs meaning that its crystal structure will be under compressive strain when grown on GaAs (Figure 2a). This has two consequences: first, there is a maximum layer thickness, smaller for higher In

content, that can be grown before the crystal structure breaks, forming dislocations. This is generally known as the Mathews-Blakeslee (MB) limit<sup>17</sup>, although it is often the case – specially for the highest In content - that the growing surface ripples and relaxes before reaching such a limit, producing the so called quantum wires (1-dimensional nanostructures) or quantum dots (0-dimensional). The second consequence is that, even if layers are kept thin, stress will accumulate as more QWs are added to the structure, leading to the same catastrophic consequence of formation of dislocations. In order to avoid this effect and been able to fabricate many QW layers with good quality – in principle, a perfect defect-free structure – the compressive strain introduced by the InGaAs can be balanced by a tensile strain in the barriers, made of GaAsP and therefore with a smaller lattice parameter than GaAs<sup>9</sup>. In a well designed strain balanced structure that alternates compressive and tensile layers (Figure 2b, top) the average stress in the structure is zero and therefore the quality of the crystal is preserved. Such stress can indeed be measured and controlled in situ with a mechano-optical stress sensor technique (MOSS), which has allowed to perfect and better understand the strain-balance process of nanostructures<sup>18,19</sup>.

From the point of view of the band structure modification, the alternating layers of low/high bandgap materials can be considered as a metamaterial with an effective bandgap defined by the position of the ground energy levels of electrons and holes in the conduction and valence band, respectively (Figure 2b, bottom). In the extreme case of very narrow barriers, the energy levels of adjacent QWs couple and form mini-bands<sup>20</sup>.

## 2. CHALLENGES FOR QW SOLAR CELLS

Two are the challenges that QWs need to face in order to achieve the optimal properties needed in near 50% efficient MJ solar cells: absorb enough amount of light and collect all photogenerated carriers. While achieving these goals are general issues in any solar cell, for the QW-based structures the challenges they represent do not have a simple answer.

### 2.1 Confined levels and absorption spectrum

The absorption of light in QWs depends on the position of the energy levels for electrons and holes, the allowed transitions between those levels and the strength of those transitions. While a detailed description of the physics of QWs is beyond the scope of this paper – a detailed analysis can be seen for example in reference [21] -, for their application in solar cells it is important to highlight three aspects: the dependence of the position of the energy levels with the composition/thickness of the QW material and the influence of strain in the absorption strength.

The position and composition of the QWs – and of the barrier – define the absorption edge of the nanostructures. Wide and high In content wells will result in deeper energy levels and lower energy transitions (Figure 3b), desirable for MJ solar cells. However, as discussed in the previous section, maintaining a good crystal quality imposes a limit to what low energies can be achieved. Figure 3d shows the dependence of the absorption edge (black lines) and the MB limit (blue line) for a range of QW thickness and composition. As it can be seen, with this configuration it is possible to achieve the 1.18 eV absorption edge required for the 3J solar cell shown in Figure 1, but the options for reaching the 1.15 eV edge needed in the 4J device are very limited. However, the band structure of the QWs can be further engineered by introducing interlayers in between the well and the barrier material (Figure 3c). These interlayers serve to two purposes: they help to keep good material quality by avoiding intermixing of elements between the well and the barrier, and they lower the energy levels by making the confinement weaker. This can be clearly seen in the number of levels that fit inside the QW in Figure 3c and also in the absorption edges that can be achieved (Figure 3e). In this case, there are several combinations of In content and well thickness that can reach the 1.15 eV.

However, highly strained QWs have a negative effect on the strength of the light absorption: it is known that in strained materials, the effective mass of heavy holes is lower which, in turn, make the density of states in the valence band also lower. As the absorption of light depends on the density of states, strained QWs will have lower absorption. This situation is very attractive in lasers since a lower density of states results in a lower threshold current for lasing<sup>16</sup>. On the positive side, highly strained QWs are narrower, as imposed by the MB limit, and introduce less stress, meaning that a larger number of QWs can be incorporated into the same thickness of solar cell (or even smaller). The net effect, as shown by Fuji *et al.*<sup>20</sup>, is that for the same thickness of solar cell, highly strained, narrow wells will absorb more light simply because there can be more absorbing units.

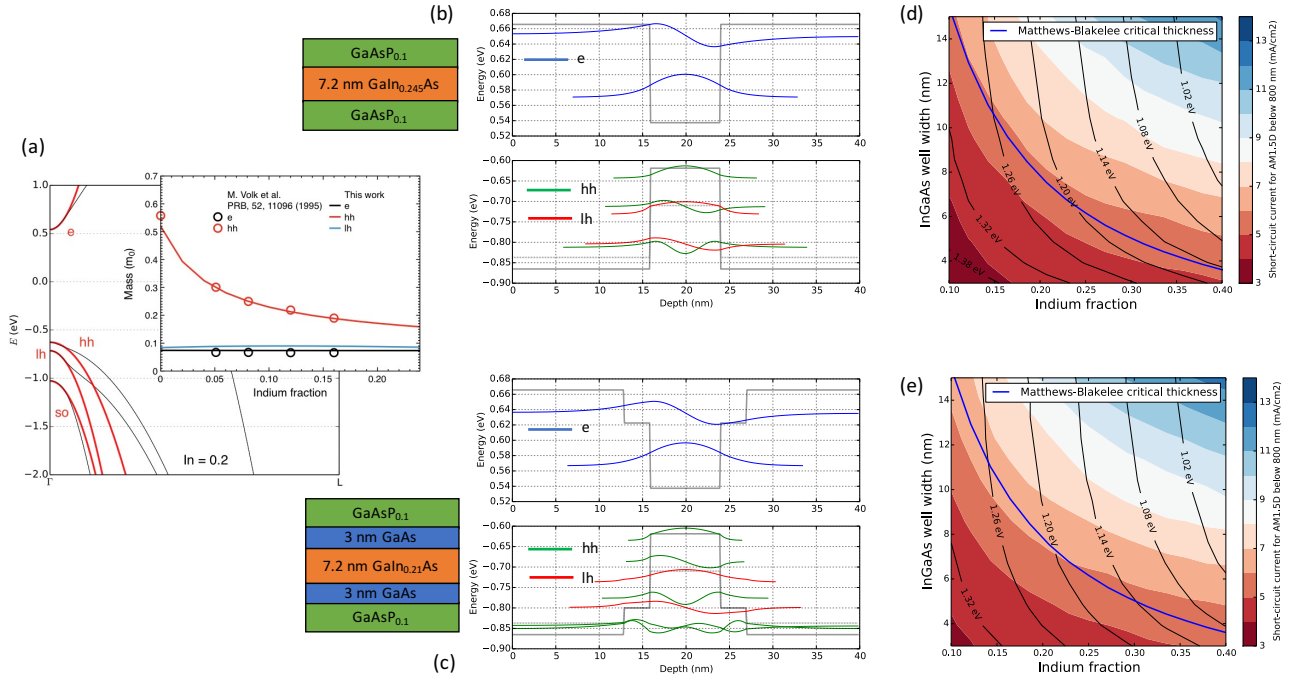


Figure 3: (a) Bulk InGaAs effective masses calculated using a 8-band kp model and comparison with experimental data<sup>22</sup>. (b) Potential profile for a In<sub>0.245</sub>GaAs/GaAsP<sub>0.1</sub> QW together with the electron and hole wavefunctions. Two confined electron levels are present in addition to three heavy hole and two light hole levels. (c) Potential profile for a In<sub>0.21</sub>GaAs/GaAsP<sub>0.1</sub> QW with 3 nm GaAs interlayers, together with the electron and hole wavefunctions. Two confined electron levels are present in addition to five heavy hole and two light hole levels. (d) and (e) shown the energy threshold of absorption (black lines) as a function of In fraction and QW width for the square and the stepped structures. The MB limit is also shown in each case: only conditions below the line can be grown. The  $J_{sc}$  for a fixed 1800nm wide MQW absorber is also shown.

## 2.2 Addressing the non-radiative losses

So far, we have focused on the absorption properties of the QWs to make an efficient junction for a MJ solar cell, either on the targets they must reach or the actual sensible values based on what can be fabricated. However, nothing has been said on the collection of the photogenerated carriers, the main challenge that MQW have to face at the moment. The problem of carrier collection is essentially associated with the non-radiative recombination, typically Shockley-Reed-Hall (SRH) recombination<sup>23</sup>. In this section we discuss some options and strategies to reduce SRH recombination in order to improve the collection of carriers out of the MQW structures.

The placement of the QWs inside the cell, closely related with carrier extraction, has been the topic of several works along the years. Nelson *et al.* found that the background doping of the intrinsic region played a key role on the process and that a careful placement of the QWs away from the region where minority carrier densities were similar helped to reduced non-radiative recombination<sup>24</sup>.

Sugiyama *et al.*, also found a strong dependence on the solar cell properties on the MQW position inside the device<sup>25</sup>. They concluded that an asymmetric placement of the MQW stack towards the p-region lead to an enhancement of the photocurrent and fill factor, in spite of a drop of the open circuit voltage. A similar analysis was made by Bailey *et al.* although in this case, the difference in the performance of solar cells with shifted QWs was related to the inhomogeneous electric field in the intrinsic region consequence of a high background doping<sup>26</sup>. All these results pointed to the importance of taking into account the different transport properties of electrons and holes, specially if background doping was present.

In practice, however, we need to keep sensible junction thickness while having good light absorption and carrier collection. So the real question is how to maximize the number of QWs in the cell at the same time that the SRH

recombination is avoided. The simple answer is to fill the intrinsic region of the solar cell with QWs except in the region where SRH recombination is higher, and only in that region, leaving a gap in the QW stack.

Figure 4 illustrates this re-design of the MQW structure. In Figure 4a we show the SRH recombination current as a function of the position inside the intrinsic region of a solar cell with 40 QWs in the center. Full details of the properties of the QWs and the structure of the cell can be found in [15]. This SRH current shows a maximum somewhere near the n-type region of the solar cell, where under the conditions of the simulation, the population of electrons and holes is similar.

In Figure 4b we show the current of the cell at maximum power point ( $I_{MPP}$ ) calculated for 1 sun of irradiance as we move the gap across the MQW structure. The number of QWs is always 40. In the example we choose a width for the gap equivalent to 10 QWs (~218 nm), which is around the width at half maximum of the SRH recombination curve in Figure 4a. The current peaks when the center of the gap is at 905 nm, leaving 34 QWs on one side and 6 QWs on the other. As expected, the optimum position of the gap coincides with the region of maximum SRH recombination. The current at that point is 6% higher than in the case of a continuous, centered QW stack, which supports the idea that a simple reorganisation of the layers helps to make more efficient devices.

By breaking the MQW into two halves, as this result suggests, we can make a more efficient use of the i-region volume, placing the QWs in all but the regions of highest recombination.

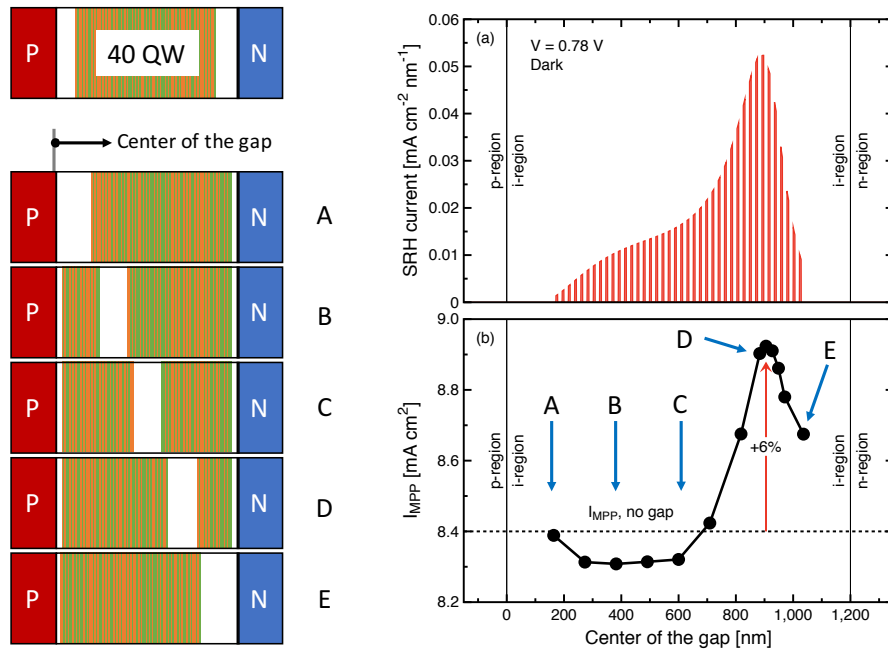


Figure 4: Left: A-E MQW structures with a gap in the stack. The total number of QWs is the same in all cases. (a) SRH recombination current for a test structure with 40 QWs symmetrically placed inside the intrinsic region of the solar cell. The SRH recombination peaks for the QWs near the n-type region. (b) Current at maximum power point  $I_{MPP}$  when a gap is left in the QW stack. When that gap coincides with the peak of the SRH recombination, structure D on the left, the  $I_{MPP}$  is maximum<sup>15</sup>.

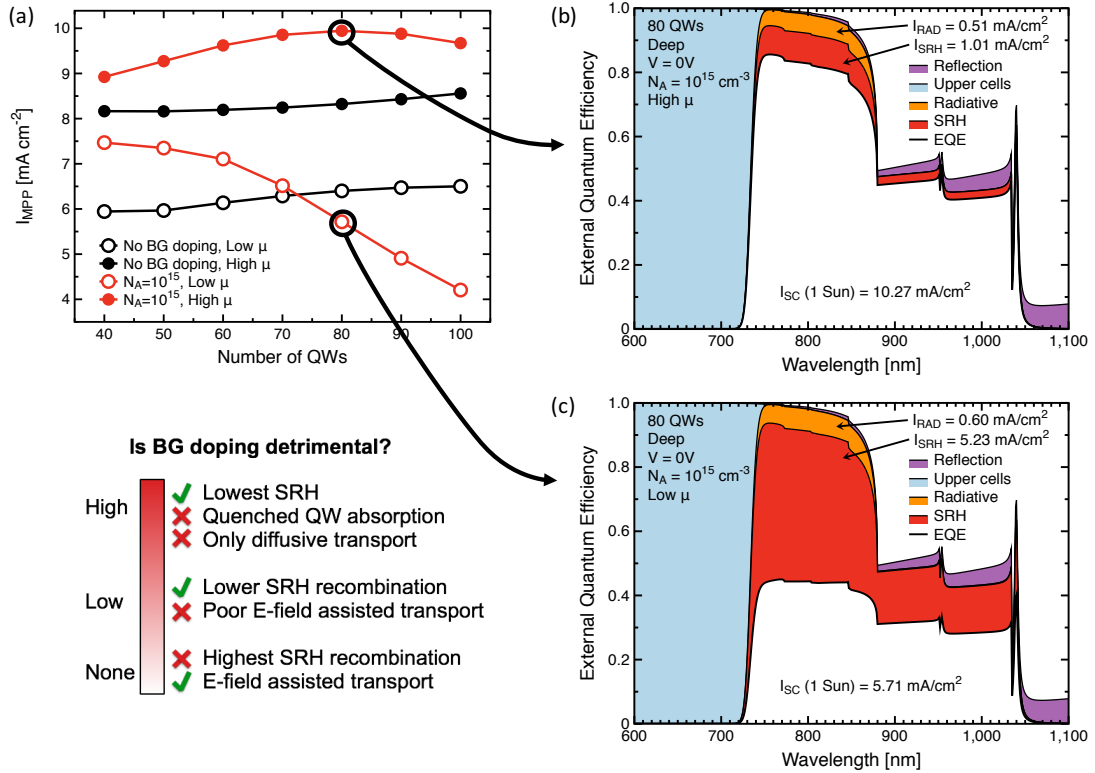


Figure 5: (a) Calculated  $I_{MPP}$  as a function of QW number for two levels of background doping and two levels of carrier mobility in the QWs. External quantum efficiency at zero bias of a solar cell with of 80 QWs in the case of having a p-type background (BG) doping of  $10^{15} \text{ cm}^{-3}$  when carrier mobilities are (b) high and (c) low. The different colors represent the main sources of losses: reflection on the front surface, absorption by the upper subcells of the multi-junction device, radiative and SRH recombination. The current lost due to the latter effects and the short circuit current produced by the cells are also included.

### 2.3 Carrier collection efficiency

Finally, it has been suggested above that a large number of QWs should provide a higher absorption and therefore higher photocurrent<sup>27,28</sup>. However, it is also found that the open circuit voltage decreases with the number of wells due to higher non-radiative dark current, balancing the benefits of including more QWs<sup>29</sup>. This effect would be more severe for deep or lower quality QWs, when dark current is higher and mobilities, lower.

On the other hand, it is generally considered desirable to have a negligible background (BG) doping in the i-region of the solar cell, keeping a high electric field in the MQW region aiding carrier collection. If such doping is relatively high –  $10^{15}$  to  $10^{16} \text{ cm}^{-3}$  are common levels –, part of the QWs might be in a flat band region and transport has to proceed diffusively only. This is highly detrimental for the solar cell performance if mobilities are low. However, it is important to note that a truly intrinsic region has much higher SRH recombination – even without the presence of QWs – than a slightly doped one given the similarity between the concentration of electrons and holes in the former.

The conclusion of these two observations is that a slight background doping might actually be beneficial and allow for higher solar cell performances if the MQW structure can keep “reasonable” mobilities. The exact minimum value depends on the intended number of QWs, as we will show next, but several hundreds of  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , close to bulk materials such as GaInP, seems to be essential. In Figure 5a we test this hypothesis by plotting the  $I_{MPP}$  as a function of QW number in four cases: high and low mobilities with low ( $10^{15} \text{ cm}^{-3}$ ) and negligible BG doping. The low mobility scenario uses mobility values inside the QWs ten times lower than the high mobility one<sup>15</sup>.

Figure 5b and 5c show the simulated QE when including 80 QWs in the case of having some BG doping for the high and

low mobilities scenarios, representing the two extreme cases. When mobility is high, most photogenerated carriers in the QWs are collected and those photogenerated in the host material (GaAs) can cross safely the QW region, mostly by simple diffusion. Losses due to SRH recombination are small. If mobilities are low, the carriers will not be able to cross the QW region and more than half will recombine non-radiatively. For the same mobility, a truly intrinsic region will aid carrier collection due to the higher electric field. However, that same true intrinsic region will be detrimental in the case of high mobility because of the enhancement of the SRH recombination.

Knowing and controlling the background doping – incorporating it intentionally if necessary – is therefore essential, but maybe more important is to know and understand the mobilities of electrons and holes when they move across a region with QWs in order to choose the best design.

A great experimental and theoretical effort is being done in this line, using the time of flight technique to estimate the mobilities of electrons and holes<sup>30</sup>. The values obtained by Toprasertpong et al. are around  $0.3 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ , for both electrons and holes, 2-3 orders of magnitude lower than those used in the above calculations. However, it should be noted that the meaning of the mobility is different in both cases: here we exclude the carrier scape time from the mobility whereas Toprasertpong considers an effective media and, therefore, includes all trapping-detrapping process, being reasonable to obtain much lower values for the mobility.

### 3. TARGETS AND CURRENT STATUS OF THE TECHNOLOGY

#### 3.1 Target performance for maximum efficiency

The question of light absorption in MJ solar cells has often been addressed from the point of view of tailoring the absorption edge of the host cell to a more advantageous, lower value. As discussed before, for a 3J device with a germanium bottom cell, an optimum band gap combination under AM1.5D solar spectrum at 1000 suns would be around 1.19 eV – 1.75 eV for the middle – top cells, respectively (Figure 1). However, Browne *et al.* showed that the optimum bandgap in a QW solar cell was indeed dependent on the quantum efficiency of the QWs, being higher if that efficiency was below certain value<sup>1</sup>. As we will discuss in the next section, although the quantum efficiency (QE) of a MQW structure can reach up to 75%, state of the art MQW solar cells have more often values between 40%-60%. In any case, far from the 90% assumed in the calculations.

New calculations have been made to account for this limited QE of the QWs in the case of the 3J and 4J devices (Figure 4). The host material of the QW subcell is assumed to have the absorption edge at 1.4 eV, close to that of  $\text{In}_{0.01}\text{GaAs}$ , which is lattice matched to Ge. Light not absorbed by the QWs passes through and can be used by the Ge junction. The insets in Figure 4 illustrate this situation.

For the case of the 3J device, it can be seen that the optimal absorption edge of the QW when the QE is below 35% stays almost constant at 1.35 eV and that the associated efficiency improvement is very small. Once the QE reaches 40%, the optimal bandgap jumps suddenly down to 1.12 eV, at the same time that the bandgap of the top cell drops to 1.8 and the efficiency improvement becomes steeper. As the QE of the QWs gets closer to 90%, the optimal bandgaps and the efficiency described above are recovered.

The explanation behind the jump at 35% of QE is related with the shape of the solar spectrum: between 1.27 eV and 1.33 eV the spectral irradiance of the Sun is much lower consequence of absorption by water in the atmosphere<sup>31</sup>. Therefore, extending the absorption edge to lower energies in order to collect more light does not compensate the associated loss in voltage. Only when the QE is high enough, extending the absorption edge down to 1.12 eV becomes beneficial, covering all the solar spectrum up to the next dip due to water absorption, between 1.06 eV 1.11 eV.

The same trends described for the 3J can be observed for the 4J optimization (Figure 4b). Sudden jumps in the optimal absorption edge of the QWs as the QE increases are associated to the dips in the solar spectrum, in this case covering also the second one in order to reach the limit of the third water absorption region that starts at 0.93 eV. However, as it has been discussed, reaching these energies with strain balanced quantum wells is very challenging, when not impossible. As a consequence, in order to have target efficiencies meaningful for QWs, we have recalculated the optimal absorption edges when the QW absorption edge is fixed at 1.15 eV. The resulting efficiency (dashed, black line in Figure

4b) is, not surprisingly, lower than in the case of complete optimization, but still very high. For QW with 90% of QE, the efficiency is 51.3%, as discussed in the first section, but even for QE of just 50%, this can be as high as 48%.

These results prove that even in the case of incomplete light absorption by the QWs, very high conversion efficiencies can indeed be achieved, justifying further research in the field. Table I shows the target short circuit current ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ) and fill factor (FF) that a QW solar cell with QEs of 50% and 90% (ideal case) should have for the 3J and the 4J structures. The values are calculated for 1 sun of intensity under the AM1.5D spectrum filtered by the upper cells of the structure.

It should be noted that all these calculations are based on the search of a mathematical maximum of the efficiency. However, as it can be seen in the color plots of Figure 1, there is always a region around the maximum where efficiency is very similar and that might allow for an even greater flexibility when choosing the absorption edges of both the QWs and the upper sub-cells.

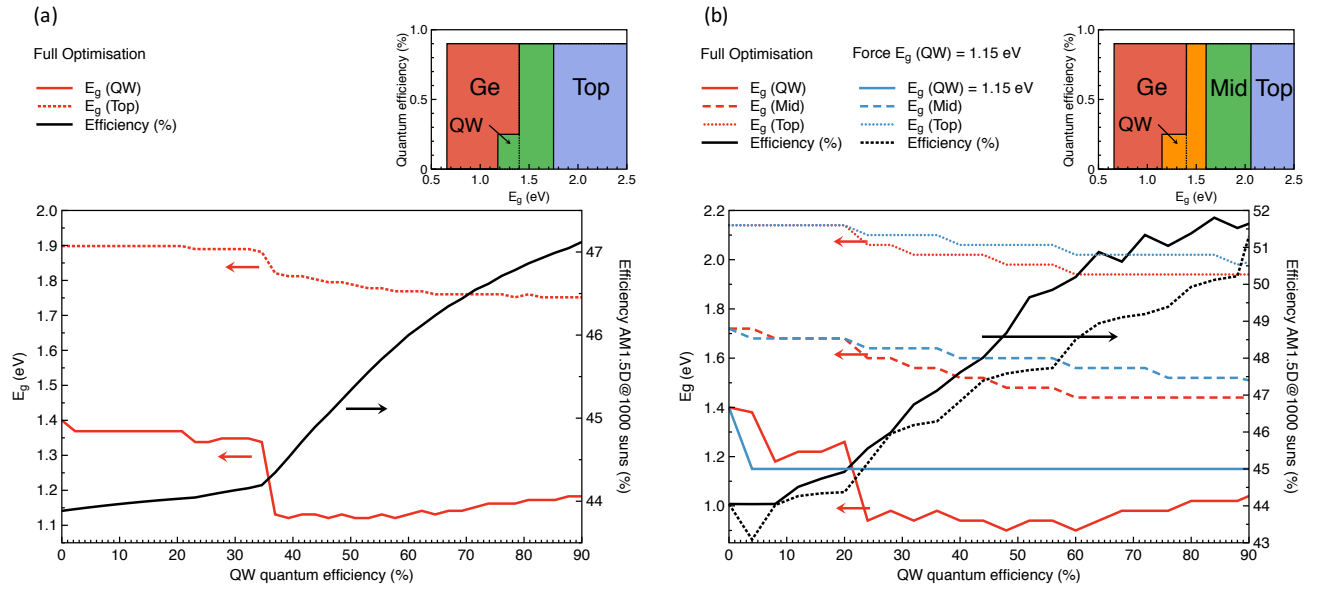


Figure 4: Calculated optimal bandgap combinations for MJ solar cells with QWs as a function of their quantum efficiency. (a) 3J device with QWs in the middle junction. (b) 4J device with QW in the lower-middle junction. The inset in each case shows a schematic representation of the quantum efficiencies of each subcells. For the 4J device we also illustrate the optimal bandgaps when the QW absorption edge is fixed at 1.15 eV, as an achievable value for strain-balanced QWs. In both cases, the host material of the QW cell is assumed to absorb from 1.4 eV.

Table 1: Calculated target  $I_{sc}$ ,  $V_{oc}$  and FF at AM1.5D and 1 sun of intensity necessary to achieve the maximum efficiency in the 3J and 4J scenarios.  $E_g$  and QE refer to the bandgap and the QE efficiency of the QWs.  $\eta$  represents the efficiency of the whole MJ device.

|           | $E_g$<br>(eV) | $\eta$<br>(%) | QE<br>(%) | $I_{sc}$<br>(mA/cm <sup>2</sup> ) | $V_{oc}$<br>(V) | FF<br>(%) |
|-----------|---------------|---------------|-----------|-----------------------------------|-----------------|-----------|
| <b>3J</b> | 1.12          | 45.3          | 50        | 15.8                              | 0.764           | 77.5      |
|           | 1.19          | 47.1          | 90        | 16.6                              | 0.809           | 78.4      |
| <b>4J</b> | 1.15          | 47.7          | 50        | 10.7                              | 0.776           | 77.4      |
|           | 1.15          | 51.3          | 90        | 11.9                              | 0.766           | 77.4      |

### 3.2 State of the art MQW solar cells

In general, achieving 1.2 eV or lower energies with strain-balanced QWs on GaAs substrates is challenging and requires the growth of deep strain balanced nanostructures and complex multi-step heterostructures, as it has been pointed out in section 2. This aggressive growth can be detrimental for the material quality, the carrier extraction and its transport to the contacts which suggests that it is necessary to consider a trade-off between extending the absorption edge and keeping good transport properties in order to get the highest efficiency.

Several of the techniques described so far have been applied to practical structures with very promising results. Fujii *et al.* reported in 2013 a MQW structure with 100 periods, a QE of near 75% and with an absorption edge at 1.23 eV<sup>27</sup>. Their performance as a solar cell when illuminated with filtered light ( $E < 1.86$  eV) showed an  $I_{sc} = 12.1$  mA/cm<sup>2</sup>,  $V_{oc} = 0.823$  and FF=74.6%. This superlattice structure was made of In<sub>0.3</sub>Ga<sub>0.7</sub>As (3.5 nm) / GaAs<sub>0.6</sub>P<sub>0.4</sub> (3.0 nm) with GaAs interlayers 2.7 nm thick. The narrow, highly strained wells and barriers allow for very high light absorption in a small volume and encouraging carrier collection by tunnel transport through the thin barriers. The impact of tunnel transport has not been included in the discussion of previous sections, but it has been addressed for these type of high aspect ratio MQW structures and how they impact the solar cell properties in reference [20].

More recently, Toprasertpong et al, has reported on the extension of the absorption threshold of a MQW structure down to 1.15 eV while keeping a QE above 40% at the absorption edge<sup>32</sup>. The structure of these QWs was rather complex: it had 70 QW periods and up to 8 layers per period, including 6 interlayers with different compositions, which were responsible of extending the absorption that far in the low energy region while keeping good structural quality. It was designed to be used as lower middle junction in a 4J device and its performance when using filtered light ( $E < 1.55$  eV) showed an  $I_{sc} = 8.5$  mA/cm<sup>2</sup>,  $V_{oc} = 0.736$  and FF=65.0%. Comparing these values for those of the corresponding 1.15 eV – 50% design of Table 1, it can be seen that this MQW structure is not that far from the target parameters and it just presents a too low value for the FF. In this sense, further work enhancing the carrier collection efficiency will be necessary, although it should be noted that the FF is also influenced by the series resistance, which might be playing a role in this case.

Finally, a new type of shallow quantum wires has just been suggested as a suitable candidate for solar cells, instead of QWs. These QWRs appear spontaneously when growing QWs on a miss-oriented substrate under the correct growth conditions. It has been shown that carrier lifetime is much higher than comparable QWs, in the range of 1  $\mu$ s, and that such property could be exploited to enhance carrier collection<sup>33</sup>. The most recent results, just published, indeed showed and improvement in the FF compared with similar QWs, while keeping the same  $I_{sc}$  and  $V_{oc}$ <sup>34</sup>.

These remarkable results, on the verge of fulfilling the design targets for limited absorption QWs shown in Table 1, clearly point to the potential of the technology for high efficiency photovoltaics and they show where more work needs to be done.

## 4. CONCLUSIONS

In this work we have presented QWs as a suitable means for achieving over 50% efficient multi-junction solar cells for high concentration applications, reviewing the challenges they face and several strategies affecting the design of the MQW solar cells: enough optical absorption and good carrier collection.

SRH recombination, as the most important losses mechanism affecting the collection of photocarriers, can be controlled by a smart placement of the QWs in the structure. A novel broken MQW stack, leaving a gap in the least favorable region, can greatly reduce those losses. Placing the QWs in a lightly doped region also reduces SRH as long as carrier mobilities are sufficiently high, something that is still to be demonstrated.

On the optical absorption side, it has been shown that more QWs in a structure increases the current produced by the cell when the background doping and the mobilities are considered in order to chose the correct number wells and they are placed in the most favorable location. Highly strained QWs, although have lower individual optical absorption, allow for a larger number of units in the structure, increasing the overall absorption.

Finally, we have shown that even with limited absorption and QE as low as 50%, very high efficiencies in the vicinity of 48% can be achieved in QW-based MJ solar cells, encouraging further work in this type of nanostructures for photovoltaics.

## REFERENCES

- [1] Adams, J. G. J., Browne, B. C., Ballard, I. M., Connolly, J. P., Chan, N. L. A., Ioannides, A., Elder, W., Stavrinou, P. N., Barnham, K. W. J., et al., “Recent results for single-junction and tandem quantum well solar cells,” *Prog. Photovolt: Res. Appl.* **19**(7), 865–877 (2011).
- [2] Browne, B., Lacey, J., Tibbits, T., Bacchin, G., Wu, T.-C., Liu, J. Q., Chen, X., Rees, V., Tsai, J., et al., “Triple-junction quantum-well solar cells in commercial production,” presented at 9th International Conference on Concentrator Photovoltaic Systems: CPV-9, 2013, 3–5, AIP.
- [3] Green, M. A., Emery, K., Hishikawa, Y., Warta, W., Dunlop, E. D., “Solar cell efficiency tables (version 43),” *Prog. Photovolt: Res. Appl.* **22**(1), 1–9 (2013).
- [4] Jones, R. K., Ermer, J. H., Fetzer, C. M., King, R. R., “Evolution of Multijunction Solar Cell Technology for Concentrating Photovoltaics,” *Jpn. J. Appl. Phys.* **51**(10), IOP Publishing (2012).
- [5] Philipps, S. P., Guter, W., Welser, E., Schöne, J., Steiner, M., Dimroth, F., Bett, A. W., “Present Status in the Development of III–V Multi-Junction Solar Cells,” [Next Generation of Photovoltaics], Springer Berlin Heidelberg, Berlin, Heidelberg, 1–21 (2012).
- [6] Dimroth, F., Grave, M., Beutel, P., Fiedeler, U., Karcher, C., Tibbits, T. N. D., Oliva, E., Siefer, G., Schachtner, M., et al., “Wafer bonded four-junction GaInP/GaAs//GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency,” *Prog. Photovolt: Res. Appl.* **22**(3), 277–282 (2014).
- [7] Derkacs, D., Jones-Albertus, R., Suarez, F., Fidaner, O., “Lattice-matched multijunction solar cells employing a 1 eV GaInNAsSb bottom cell,” *J. Photon. Energy* **2**(1), 021805–1–9 (2012).
- [8] Barnham, K. W. J., Duggan, G., “A new approach to high-efficiency multi-band-gap solar cells,” *J. Appl. Phys.* **67**(7), 3490–3495 (1990).
- [9] Ekins-Daukes, N. J., Kawaguchi, K., Zhang, J., “Strain-Balanced Criteria for Multiple Quantum Well Structures and Its Signature in X-ray Rocking Curves †,” *Crystal Growth & Design* **2**(4), 287–292 (2002).
- [10] Green, M. A., Emery, K., Hishikawa, Y., Warta, W., Dunlop, E. D., “Solar cell efficiency tables (version 46),” *Prog. Photovolt: Res. Appl.* **23**(7), 805–812 (2015).
- [11] Chan, N. L. A., Ekins-Daukes, N. J., Adams, J. G. J., Lumb, M. P., Gonzalez, M., Jenkins, P. P., Vurgaftman, I., Meyer, J. R., Walters, R. J., “Optimal Bandgap Combinations - Does Material Quality Matter?,” *IEEE J. Photovoltaics* **2**(2), 202–208 (2012).
- [12] Thomas, T., Wilson, T., Führer, M., Alonso-Álvarez, D., Ekins-Daukes, N. J., Lackner, D., Kailuweit, P., Philipps, S. P., Bett, A. W., et al., “Potential for reaching 50% power conversion efficiency using quantum heterostructures,” presented at 6th World Conference on Photovoltaic Energy Conversion, 2014, Kyoto (Japan), 1–2.
- [13] Führer, M. F., Adams, J. G. J., Barnham, K. W. J., Browne, B. C., Chan, N. L. A., Farrell, D. J., Hirst, L., Lee, K.-H., Ekins-Daukes, N. J., et al., “Extensible modelling framework for nanostructured III-V solar cells,” 2011 37th IEEE Photovoltaic Specialists Conference (PVSC), 002615–002618, IEEE (2011).
- [14] Führer, M., Farrell, D., Ekins-Daukes, N., “CPV modelling with Solcore: An extensible modelling framework for the rapid computational simulation and evaluation of solar cell designs and concepts,” presented at 9th International Conference on Concentrator Photovoltaic Systems: CPV-9, 10 February 2014, 34–37, AIP.
- [15] Alonso-Alvarez, D., Führer, M., Thomas, T., Ekins-Daukes, N., “Elements of modelling and design of multi-quantum well solar cells,” 2014 IEEE 40th Photovoltaic Specialists Conference (PVSC), 2865–2870, IEEE (2014).
- [16] Adams, A. R., “Strained-Layer Quantum-Well Lasers,” *IEEE J. Select. Topics Quantum Electron.* **17**(5), 1364–1373 (2011).
- [17] Matthews, J., Blakeslee, A. E., “Defects in epitaxial multilayers. I. Misfit dislocations,” *Journal of Crystal Growth* **27**(C), 118–125 (1974).
- [18] Alonso-Alvarez, D., Ripalda, J. M., Alén, B., Llorens, J. M., Rivera, A., Briones, F., “Strain Balanced Epitaxial Stacks of Quantum Dots and Quantum Posts,” *Adv. Mater.* **23**(44), 5256–5261 (2011).
- [19] Sugiyama, M., Sugita, K., Wang, Y., Nakano, Y., “In situ curvature monitoring for metal–organic vapor phase epitaxy of strain-balanced stacks of InGaAs/GaAsP multiple quantum wells,” *Journal of Crystal Growth* **315**(1), 1–4, Elsevier (2011).

- [20] Fujii, H., Wang, Y., Watanabe, K., Sugiyama, M., Nakano, Y., “High-Aspect Ratio Structures for Efficient Light Absorption and Carrier Transport in InGaAs/GaAsP Multiple Quantum-Well Solar Cells,” *IEEE J. Photovoltaics* **3**(2), 859–867, IEEE (2013).
- [21] Chuang, S. L., *Physics of Optoelectronic Devices*, Wiley-Interscience (1995).
- [22] Volk, M., Lutgen, S., Marschner, T., Stolz, W., Göbel, E. O., Christianen, P. C. M., Maan, J. C., “Carrier effective masses in symmetrically strained (GaIn)As/Ga(PAs) multiple-quantum-well structures,” *Phys. Rev. B* **52**(15), 11096–11104, American Physical Society (1995).
- [23] Sze, S. M., *Physics of semiconductor devices*; 2nd ed., Wiley, New York, NY (1981).
- [24] Nelson, J., Ballard, I., Barnham, K., Connolly, J. P., Roberts, J. S., Pate, M., “Effect of quantum well location on single quantum well p-i-n photodiode dark currents,” *J. Appl. Phys.* **86**(10), 5898–5899 (1999).
- [25] Sugiyama, M., Wang, Y., Choi, S., Wen, Y., Nakano, Y., “How shall we put multiple quantum wells in p-i-n structure for efficiency enhancement?,” 2010 35th IEEE Photovoltaic Specialists Conference (PVSC), 000376–000379, IEEE (2010).
- [26] Bailey, C. G., Lumb, M. P., Hoheisel, R., Gonzalez, M., Forbes, D. V., Yakes, M. K., Hubbard, S. M., Hirst, L. C., Lorentzen, J., et al., “The effects of electric field on InGaAs quantum well i-region placement in InAlGaAs solar cells,” presented at SPIE OPTO, 7 March 2014, 898104–898106, SPIE.
- [27] Fujii, H., Toprasertpong, K., Wang, Y., Watanabe, K., Sugiyama, M., Nakano, Y., “100-period, 1.23-eV bandgap InGaAs/GaAsP quantum wells for high-efficiency GaAs solar cells: toward current-matched Ge-based tandem cells,” *Prog. Photovolt: Res. Appl.* **22**(7), 784–795 (2013).
- [28] Bushnell, D. B., Tibbits, T. N. D., Barnham, K. W. J., Connolly, J. P., Mazzer, M., Ekins-Daukes, N. J., Roberts, J. S., Hill, G., Airey, R., “Effect of well number on the performance of quantum-well solar cells,” *J. Appl. Phys.* **97**(12), 124908–4 (2005).
- [29] Lynch, M. C., Ballard, I. M., Bushnell, D. B., Connolly, J. P., Johnson, D. C., Tibbits, T. N. D., Barnham, K. W. J., Ekins-Daukes, N. J., Roberts, J. S., et al., “Spectral response and I-V characteristics of large well number multi quantum well solar cells,” *J Mater Sci* **40**(6), 1445–1449, Kluwer Academic Publishers (2005).
- [30] Toprasertpong, K., Tanibuchi, T., Fujii, H., Kada, T., Asahi, S., Watanabe, K., Sugiyama, M., Kita, T., Nakano, Y., “Comparison of Electron and Hole Mobilities in Multiple-Quantum-Well Solar Cells Using a Time-of-Flight Technique,” *IEEE J. Photovoltaics* **5**(6), 1613–1620, IEEE (2015).
- [31] Committee, G., “Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37 Tilted Surface.”
- [32] Toprasertpong, K., Fujii, H., Thomas, T., Führer, M., Alonso-Alvarez, D., Farrell, D. J., Watanabe, K., Okada, Y., Ekins-Daukes, N. J., et al., “Absorption threshold extended to 1.15 eV using InGaAs/GaAsP quantum wells for over-50%-efficient lattice-matched quad-junction solar cells,” *Prog. Photovolt: Res. Appl.*, n/a–n/a (2015).
- [33] Alonso-Álvarez, D., Thomas, T., Führer, M., Hylton, N. P., Ekins-Daukes, N. J., Lackner, D., Philipps, S. P., Bett, A. W., Sodabanlu, H., et al., “InGaAs/GaAsP strain balanced multi-quantum wires grown on misoriented GaAs substrates for high efficiency solar cells,” *Appl. Phys. Lett.* **105**(8), 083124–083126 (2014).
- [34] Sugiyama, M., Fujii, H., Katoh, T., Toprasertpong, K., Sodabanlu, H., Watanabe, K., Alonso-Alvarez, D., Ekins-Daukes, N., Nakano, Y., “Quantum Wire-on-Well (WoW) Cell with Long Carrier Lifetime for Efficient Carrier Transport” *Prog. Photovolt: Res. Appl.* **n/a**, n–a (2016).